

## CHEMICAL ANALYSIS

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# CHEMICAL ANALYSIS

A SERIES OF MONOGRAPHS ON  
ANALYTICAL CHEMISTRY AND ITS APPLICATIONS

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## Volume III

*Colorimetric Determination of Traces of Metals*

By E. B. SANDELL, PH.D.

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# COLORIMETRIC DETERMINATION of TRACES of METALS

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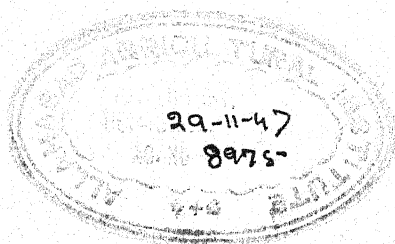


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## PREFACE

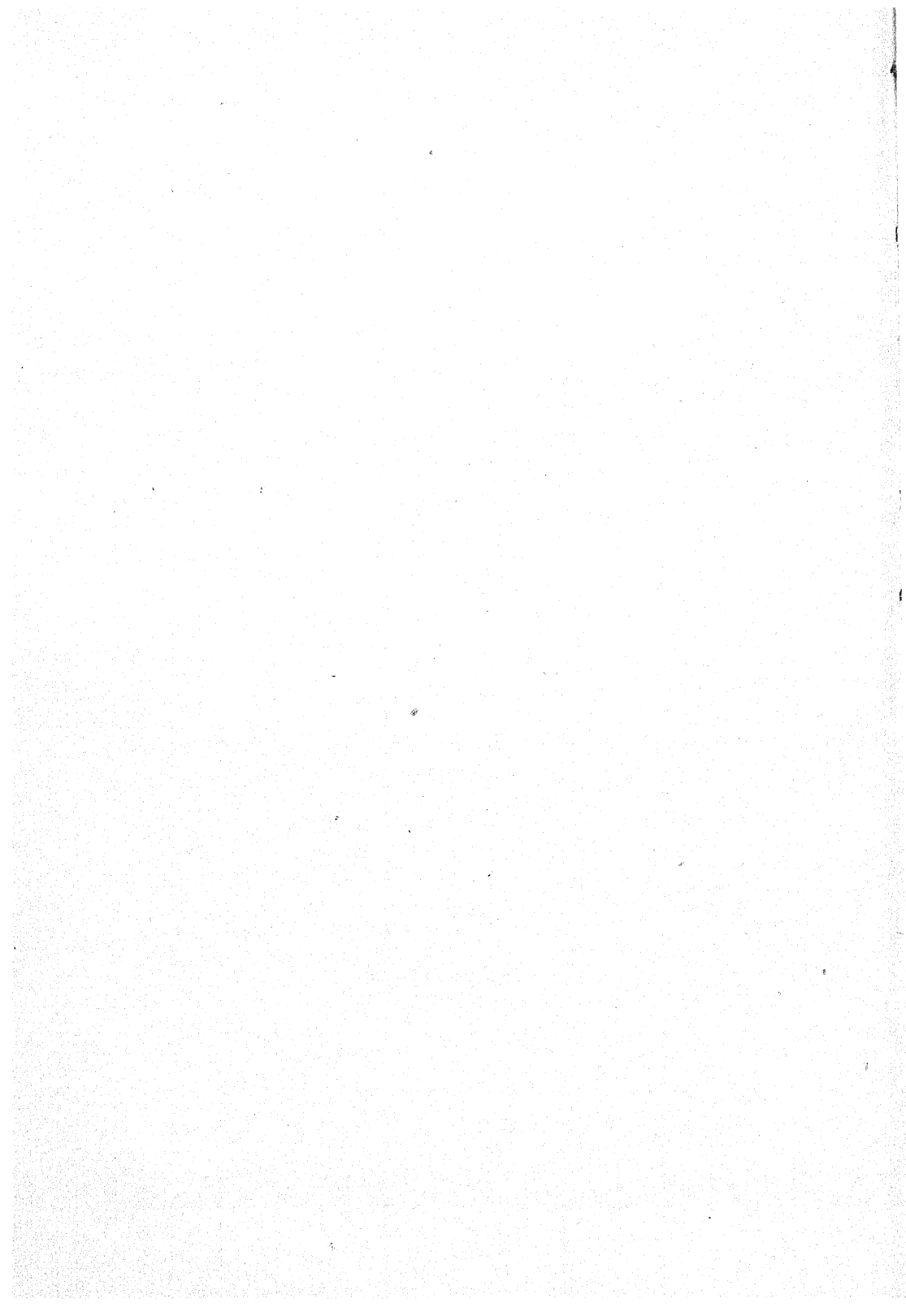
The colorimetric determination of traces of elements, especially of metals, has made great advances in recent years and it seemed to the writer that it would be useful to have available a collection of modern methods in this field of analysis. This book is the result of an attempt in this direction. It is not intended to be an encyclopaedia of methods for the colorimetric determination of small amounts of metals. The aim has been rather to present a limited number of methods which at the present time appear to be best suited for dealing with traces of metals. No one reagent is necessarily the best for the determination of an element in all kinds of samples or under all conditions, and consequently two or three methods are sometimes described in greater or less detail for a number of the metals. A few fluorimetric methods are included. The treatment is to a considerable extent based on the experience of the writer in testing or using various methods.

Anyone who surveys the methods of colorimetric trace analysis must experience a feeling of satisfaction arising from the many sensitive reactions available and, on the other hand, of something close to dismay at our imperfect knowledge of the application of these reactions. The effect of foreign elements on a particular color reaction is frequently poorly known and the prevention of the interference of foreign substances has, for the most part, been incompletely studied. Methods for the separation of traces are but poorly developed or even non-existent for many elements. The user of this book is likely to find many of his questions in this phase of trace analysis unanswered in the present treatment. It is to be hoped that the workers of the future will be willing to devote as much of their energies to this prosaic aspect of the subject as to the more inviting one of searching for new reagents.

I am greatly indebted to Professor I. M. Kolthoff for reading the manuscript and offering suggestions; I also wish to thank Messrs. Arthur Anderson, George Matsuyama, Robert W. Perlich, and Geo Safranski, for reading and commenting on portions of the manuscript.

E. B. SANDELL

Minneapolis, Minn.  
February 1944



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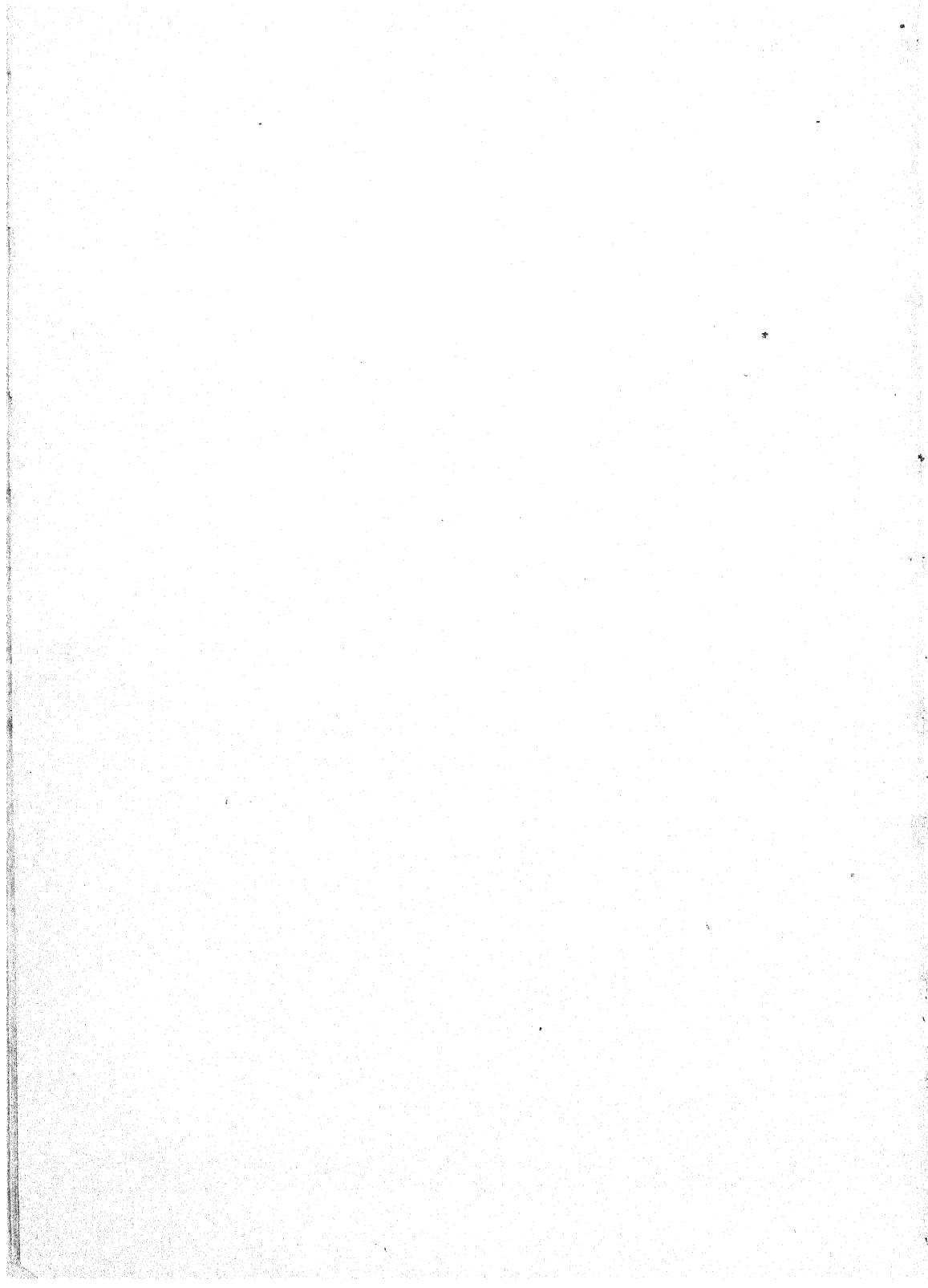
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**GENERAL PART**

**COLORIMETRIC TRACE ANALYSIS**





## CHAPTER I

### TRACE ANALYSIS

On the basis of their relative amounts, the constituents of a sample can be divided into the *macro* and the *micro* as shown in the lower part of Fig. 1. A macro constituent is here defined as one making up more than 0.01 per cent of the sample, and a micro constituent as one occurring to the extent of 0.01 per cent or less. A micro constituent may also be called a *trace* constituent.

Originally *trace* in the chemical sense meant a quantity of a constituent so small that it either could not be determined, or was thought not worth determining. Today the term has a rather different meaning, and in its general sense signifies a minute amount of a constituent which usually can be determined, and which it frequently is necessary to determine with some degree of accuracy. Just how low the percentage of a constituent must be before it can be called a trace is a matter of somewhat arbitrary definition. In this connection a statement made by Hillebrand<sup>1</sup> with reference to rock analysis is of interest. He says: "It may be said with regard to the use of the word 'trace' that the amount of a constituent thus indicated is supposed to be below the limit of quantitative determination in the amount of sample taken for analysis. It should in general, for analyses laying claim to completeness and accuracy, be supposed to indicate less than 0.02 or even 0.01 per cent." Since 0.01 per cent more or less marks the lower limit of gravimetric or volumetric methods as commonly applied, we may take this figure as indicating the approximate upper limit of a trace constituent. There is no necessity for making the boundary a rigid one. It is sometimes convenient to consider as a trace constituent one that occurs to the extent of a few hundredths of a per cent. Thus in silicate rocks copper usually falls in the range 0.001 to 0.05 per cent, and it is permissible to speak of copper as a trace constituent in this class of material.

To lessen the abruptness of transition from micro to macro constituents, it is convenient to subdivide the latter into a major and minor class. A minor macro constituent may be assigned the range 0.01 to 1 per cent. It has, at least in its lower range, a certain similarity to a micro constituent, and the methods used in trace analysis are often applied in its determination.

<sup>1</sup> W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Survey Bull.*, 700, 32 (1919). Cf. W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*. Wiley, New York, 1929; p. 659.

It has been suggested<sup>2</sup> that the concentration of a constituent in a sample can conveniently be expressed in terms of a percentage exponent,  $pP$ , defined as  $-\log P$ , where  $P$  is the percentage of the constituent. Or one may express the concentration in terms of the weight fraction of the sample ( $100\% \equiv 1$ ) and obtain a concentration exponent defined as  $-\log C$ ,  $C$  being the fraction of the constituent in the sample.<sup>3</sup> A macro constituent would then have a  $pC$  ranging from 0 to 4, and a micro constituent a  $pC$  greater than 4. In this connection it may be mentioned that it is frequently desirable to report the result of a trace analysis in parts per million, this being a convenient unit of expression.

The lower limit of a trace constituent is zero, but the lower limit of a trace analysis is set by the sensitivity of the method. In a good many cases the sensitivity and specificity of a trace method are sufficient to meet rather exacting demands. For example, it may be necessary to determine amounts of iron as small as  $10^{-5}$  mg. per liter ( $1:10^{11}$ ) of water in hydrobiological investigations (Fig. 1), and this has been accomplished. As little as  $10^{-6}$  per cent of the platinum metals has been determined in a 2 g. sample of silicate rock.<sup>4</sup>

The essential feature of a trace analysis is not the determination of a minute quantity of a substance, but the determination of such a quantity in the presence of an overwhelming quantity of other substances which may seriously affect the reaction involving the trace constituent. A trace analysis has the characteristics of both macro and micro analysis. The size of sample and sometimes the preliminary steps of a trace analysis are similar to those of macro analysis. Frequently a trace analysis requires a larger sample ( $> 1$  gram) than is used in macro analysis. In special cases, samples weighing several hundred kilograms have been taken. The final step in a trace analysis may be more micro than the usual micro analysis, in which  $1 \gamma$  is usually the limit of accuracy striven for. Many colorimetric methods enable  $1 \gamma$  or less of a constituent to be determined with an accuracy of 5 or 10 per cent, and the same is true of spectrochemical determinations.

A consideration of the distribution of trace elements in nature lies beyond the scope of this book but it may be of interest to give a table of the abundance of the rarer elements in igneous rocks and in primary sulfides (Table 1). The average content of the elements in the earth's crust is for most elements the same as their abundance in the igneous rocks. Many

<sup>2</sup> I. M. Kolthoff, Oral communication.

<sup>3</sup> Geochemists have long been accustomed to expressing the abundance of an element in this manner.

<sup>4</sup> G. Lunde and M. Johnson, *Z. anorg. allgem. Chem.*, **172**, 167 (1928).

of the so-called rare elements are as abundant as those which are usually considered common. Germanium is as abundant as arsenic, gallium as abundant as lead, cerium as abundant as zinc, scandium more abundant than mercury or bismuth, etc. From the igneous rocks the rarer elements

TABLE 1  
ABUNDANCE OF SOME OF THE RARER ELEMENTS  
(All figures are in p.p.m.)

	Igneous rocks <sup>a</sup>	Primary sulfides <sup>b</sup>		Igneous rocks <sup>a</sup>	Primary sulfides <sup>b</sup>
Ag	0.1	10	Mo	2.5	20
As	5	60	Ni	80	31400
Au	0.005	0.2	P	800	
B	3		Pb	15	100
Ba	250		Pd	0.01	4
Be	6		Pt	0.005	2
Bi	0.2	2	Rb	310	
Cb	20		Re	0.001	0.02
Cd	0.15	20	S	520	
Ce	46		Sb	1(?)	1
Cl	480		Sc	5	
Co	23	2100	Se	0.09	200
Cr	200	20	Sn	40	50
Cs	7		Sr	150	
Cu	70	10900	Ta	15(?)	
F	300		Te	0.002(?)	2
Ga	15	2	Th	11.5	
Ge	7	10	Ti	4400	
Hf	4.5		Tl	0.3	1
Hg	0.5	0.02	U	4	
I	0.3		V	150	40
In	0.1	0.7	W	69	2
La	18		Y	21	
Li	65		Zn	80	8500
Mn	1000	800	Zr	220	

<sup>a</sup> Figures are mostly from V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente, IX. Die Mengenverhältnisse der Elemente und der Atom-arten", *Skrifter Norske Vidensk.-Akad. i Oslo I. Mat. Natur. Klasse*, No. 4, 99 (1937). The values for Cd, Cu, Mo, Ni, Pb, and Zn are from estimates by E. B. Sandell and S. S. Goldich, *J. Geol.*, 51, 181 (1943).

<sup>b</sup> Values found by I. and W. Noddack, *Z. physik. Chem.*, A 154, 232 (1931), on a composite sample of 35 pyrrhotites, 10 pyrites, 8 pentlandites, and 14 nickel-pyrites.

find their way by a longer or shorter route into plant and animal matter, and many are markedly enriched in the living material in the process. The important role played by trace elements in life processes is now well realized and their determination is of practical as well as of scientific interest.

### I. Methods of Trace Analysis

A list of the methods which are or have been used in trace analysis would be a list of the methods used in general chemical analysis. Traces of elements have been determined even by gravimetric methods. For example, less than 0.001 per cent of gallium in aluminum has been determined gravimetrically by taking a 50 g. sample.<sup>5</sup> Titrimetric methods can at times render good service in trace analysis (determination of iodine, silver, etc.), especially when the end point is found potentiometrically. The new technique of amperometric titrations may find application.<sup>6</sup> Extractive titration with an organic solvent solution of dithizone (p. 72) is sometimes used in determining traces of heavy metals. When it is necessary, however, to determine very small quantities of a constituent, methods other than the gravimetric or volumetric are usually preferred, and these will be briefly discussed.

The methods commonly applied in the determination of traces may be divided into those that are of general applicability, and those that can be used only for a more or less restricted number of elements at the present time. In the latter class are methods based on measurement of radioactivity and catalytic activity,<sup>7</sup> and certain microscopical methods involving the measurement of the diameter of a precious metal bead<sup>8</sup> obtained by cupellation, or of a mercury globule.<sup>9</sup>

In the class of general methods we have photometry (colorimetry, spectrophotometry, nephelometry, and turbidimetry), optical and X-ray spectrography, and polarography.<sup>10</sup> Methods based on fluorescence may also be included here. At the present time there are comparatively few procedures for the determination of elements based on fluorescence, but it

<sup>5</sup> J. A. Scherrer, *J. Research Natl. Bur. Standards*, **15**, 585 (1935).

<sup>6</sup> See Chapter XXXIII of I. M. Kolthoff and J. J. Lingane, *Polarography*. Interscience, New York, 1941.

<sup>7</sup> The determination of the concentration of a substance exerting a catalytic effect on a reaction otherwise proceeding very slowly may often be effected through the agency of colorimetry, or more generally, photometry. An example is given on p. 379. Such catalytic methods may have extraordinary sensitivity. Thus as little as  $10^{-6}$   $\gamma$  Fe per ml. of saturated ammonium thiocyanate solution can be detected by the appearance of a pink color when the solution is exposed to sunlight (B. S. Sharma, *J. Soc. Chem. Ind.*, **48**, 336 T (1929)). This concentration corresponds to 1  $\gamma$  Fe in a cubic meter of solution.

<sup>8</sup> F. Haber, *Angew. Chem.*, **40**, 303 (1927) (determination of the gold content of sea water).

<sup>9</sup> A. Stock, *Ber.*, **71**, 550 (1938).

<sup>10</sup> For the latter see I. M. Kolthoff and J. J. Lingane, *Polarography*. Interscience, New York, 1941.

may be expected that in the course of time such methods will increase in number (*cf.* p. 65).

Present day trace analysis relies chiefly on colorimetry and spectrography, although polarographic methods are being applied to an increasing extent. A few words may be said about the comparative merits of colorimetry (including spectrophotometry) and emission spectrography in trace analysis. Spectrography can be applied to the determination of any element, although with varying sensitivity. For some elements there are no colorimetric methods, and for others the methods are not sufficiently sensitive for use in trace analysis. A great advantage of spectrographic determinations is the relatively minor influence of the other constituents of the sample in many cases. Separations are the rule rather than the exception in practical colorimetric determinations, while the reverse is true of spectrochemical determinations.

There is often less difference than usually supposed in the concentration sensitivity of spectrochemical and colorimetric methods. A small sample is ordinarily used in spectrography and this tends to increase the percentage of the element that can be determined, even though the absolute sensitivity is high. In a colorimetric determination the size of the sample taken can be 100 times as large as in an ordinary spectrographic determination, and thus the higher relative or concentration sensitivity of a colorimetric method may counterbalance the higher absolute sensitivity of a spectrographic method. If the amount of sample available is limited, the relative sensitivity of a spectrochemical method may, of course, greatly exceed that of a colorimetric method, but the situation is frequently reversed if a gram or two of sample is available.

Some comparisons between spectrochemical and colorimetric methods as regards sensitivity may be interesting. Owens<sup>11</sup> has given the following values for the average absolute sensitivity of various types of excitation:

Direct current arc	$10^{-5}$ to $10^{-4}$ mg. metal on electrode
Cathode layer of direct current arc	$10^{-6}$ to $10^{-5}$ mg.
High-voltage, alternating current arc	$10^{-6}$ to $10^{-5}$ mg.
Direct current condensed spark	$10^{-6}$ to $10^{-4}$ mg.

The practical sensitivity of some delicate color reactions corresponds to  $10^{-4}$  mg. or less (for example dithizone as reagent for Cu, Pb, Zn, Cd, etc.). *Cf.* Table 4, p. 38.

Owens gives the following figures for the lower limits of determination

<sup>11</sup> J. S. Owens, *Ind. Eng. Chem., Anal. Ed.*, **11**, 61 (1939).

of certain metals in 25 per cent sodium hydroxide (one drop of solution corresponding to 12 mg. NaOH evaporated on electrodes):

Al	$5 \times 10^{-5}\%$
Ca	$4 \times 10^{-5}\%$
Mg	$3 \times 10^{-5}\%$
Cr	$2 \times 10^{-5}\%$
Cu	$1 \times 10^{-5}\%$
Fe	$1 \times 10^{-5}\%$
Ni	$8 \times 10^{-5}\%$
Pb	$2 \times 10^{-5}\%$
Sr	$1 \times 10^{-5}\%$

By using 10 ml. of solution, these limits can be equaled or exceeded by colorimetric methods for copper, nickel, and lead and possibly some of the other metals. Traces of calcium and strontium cannot be determined at all by colorimetric methods. A great advantage of a spectrographic method in an analysis such as this is the possibility of determining all of these elements (and others) at one and the same time.

Hess, Owens, and Reinhardt<sup>12</sup> have described a spectrographic procedure for traces of metallic impurities in organic materials, in which a 0.4 g. sample is wet-ashed and 0.03 ml. of solution corresponding to 30 mg. of sample, is evaporated on an electrode and the residue arced with high-voltage alternating current. The lower limit was 0.0001 per cent for Al, Ca, Cu, Fe, Pb, Mg, Mn, Ni, Sr, Sn and 0.0005 per cent for Zn. The errors ranged from 0 to 50 per cent (latter with Zn) in the range 0.0005 to 0.005 per cent metal, with an average error of 12 per cent. For the metals Cu, Fe, Pb, and Ni comparable results can be obtained by colorimetric methods, and better results should be possible for zinc, but of course with a larger sample and a much greater expenditure of time.

In the analysis of silicates the limits of determination of some metals by the spectrographic method (cathode layer of direct current arc) are relatively high as the following table shows:<sup>13</sup>

Element	Lowest concentration determined, per cent
Li	0.00005
Be	0.00036
La	0.00085
Co	0.0037
Ni	0.0005

<sup>12</sup> T. M. Hess, J. S. Owens, and A. G. Reinhardt, *Ind. Eng. Chem., Anal. Ed.*, **11**, 646 (1939).

<sup>13</sup> L. W. Strock, *Spectrum Analysis with the Carbon Arc Cathode Layer*. A. Hilger, London, 1936.

It is stated that a single spectrum gives a possible error of 25 per cent, while the average of four spectra decreases the error to about 5 per cent. For comparison it may be noted that colorimetric methods are available for the determination of nickel and cobalt in a 0.5 g. sample of silicate which have a lower limit of 0.0001 per cent, and allow the determination of 0.001 per cent of these metals with an error of approximately 10 per cent. By a fluorescence method as little as 0.0002 per cent of beryllium can be detected in silicates. On the other hand there are no sensitive colorimetric methods for lithium and lanthanum in silicates.

By a special technique involving fractional distillation, certain relatively easily volatile metals such as zinc, cadmium, mercury, indium, thallium, germanium, antimony, and bismuth may be detected spectrographically in amounts of the order of  $10^{-6}$  per cent when 1 to 3 g. of silicate sample is taken.<sup>14</sup> As yet only cadmium has been determined in such low concentrations colorimetrically.

When it is considered that colorimetric determinations can often be made with simple inexpensive apparatus usually available in most analytical laboratories, that the analyst requires no special training, that the sensitivity of modern colorimetric procedures is often very high, and that the accuracy is as good as, or even better than, that of any other applicable method, the conclusion may be drawn that colorimetry occupies an important place among the methods of trace analysis.

#### *Limits of the Methods of Trace Analysis*

In Fig. 1 the useful ranges of gravimetric, volumetric, colorimetric, and spectrographic methods are indicated. It will be understood that the diagram is a generalized representation of the limits of the methods mentioned, because obviously there can be no hard and fast boundaries. As already mentioned, gravimetric and volumetric methods have been used in trace analysis, but in the great majority of cases they are restricted to constituents in the range 0.01 to 100 per cent, and have a limited use in the range 0.01 to 0.1 or sometimes even in the range 0.01 to 1 per cent. There is nothing inherently impossible in the use of a gravimetric or volumetric method for determining a trace constituent, a micro technique being possible if the constituent can be separated from the macro constituents, but the disadvantages of such a procedure often are so great that it is only occasionally applied.<sup>15</sup>

<sup>14</sup> E. Preuss, *Z. angew. Mineral.*, **3**, 8 (1940).

<sup>15</sup> An important exception to this generalization is the determination of gold and the platinum metals by dry assaying, in which the weight of the metal bead is obtained to within 0.01 mg.

The useful range of a colorimetric method may be considered to extend from an upper limit of about 1 per cent (visual colorimetry) or 10+ per cent (spectrophotometry) down to about  $10^{-5}$  per cent. Naturally the lower limit varies with the sensitivity of the reaction, and may be much higher than  $10^{-5}$  per cent, but for many metals and metalloids there are

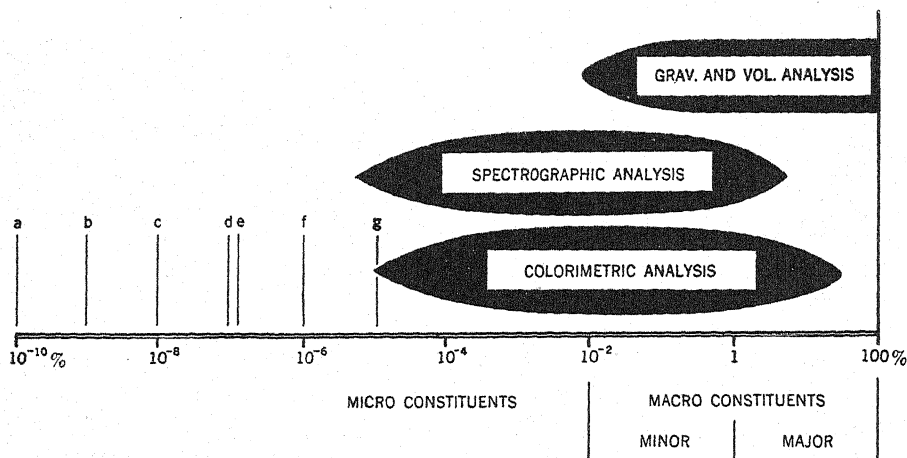


Fig. 1.—Diagram showing classification of constituents on the basis of concentration in the sample, the useful ranges of various quantitative techniques, and the sensitivity of some methods for the determination of minute traces of elements.

a. Approximate gold content of some samples of sea water as determined by the microscopical measurement of the bead of the gold isolated from two liters of sample (Haber).

b. Percentage of iron in water that can be determined colorimetrically after concentration by zeolitic exchange from a sample of 5 liters (Abrahamczik).

c. Limit of detectability of lead as chromate nephelometrically (Böttger).

d. Approximate limit of determination of selenium in 1 kg. of soil by distillation as bromide followed by reduction to selenium which is determined colorimetrically in colloidal suspension (Robinson, Dudley, Williams, and Byers).

e. Limit of determination of beryllium in aqueous solution by fluorescence with morin.

f. Approximate limit of determination of iodine in aqueous solution by catalysis of the reaction between quadrivalent cerium and arsenite.

g. Limit of colorimetric determination of palladium in a 1 g. sample of sulfide mineral.

colorimetric methods which enable percentages as low as  $10^{-5}$  to  $10^{-4}$  to be determined. It is only rarely that colorimetric methods can be, or are, applied to the determination of traces below  $10^{-5}$  per cent in a solid sample. The practical limit of the colorimetric determination of palladium in sulfides is slightly less than  $10^{-5}$  per cent, and of cadmium in silicate rocks  $5 \times 10^{-6}$  per cent. As little as  $10^{-7}$  per cent of selenium, however,



can be determined in soil. Naturally the methods of separation available and the nature of the sample will in many cases be the deciding factors in the determination of the sensitivity of the method; in the presence of large amounts of interfering substances the lower limit of a colorimetric method may be raised by a factor of 10 or 100. In the simplest possible case, a dilute aqueous solution (for example, a natural water) the limit of a colorimetric method may lie at  $10^{-8}$  or even  $10^{-10}$  per cent after isolation of the constituent. In such a case the lower limit can be pushed indefinitely downward in many instances by taking increasingly larger samples, if a good method is available for the isolation of the constituent in question.

The useful range of spectrographic methods as generally carried out is nearly coincident with that of colorimetric methods, the upper limit being 1 per cent or slightly higher, and the lower limit approximately  $10^{-5}$  per cent. With many elements a sensitivity of  $10^{-5}$  per cent cannot be reached (with some not even  $10^{-3}$  per cent), so that the limit indicated is attained only under favorable conditions as regards the nature of the sample and the element determined.

The determination of constituents occurring to the extent of 0.1 part or less per million is as a rule difficult or impossible by the usual methods of trace analysis and special procedures must in general be invoked. Fortunately the limit of most practical requirements of trace analysis lies above  $10^{-5}$  per cent and often it is considerably higher. Thus in alloy analysis, constituents rarely have to be determined in amounts less than  $10^{-3}$  to  $10^{-4}$  per cent.

The determination of a trace substance occurring to the extent of less than  $10^{-5}$  per cent in a sample will require, first, the isolation of the constituent, *i.e.*, its concentration in a small volume of liquid or solid, with or without complete separation from other constituents of the sample, and second, the determination of the constituent in the enriched phase by a method yielding a high absolute sensitivity. Spectrographic methods should be especially suitable for the purpose since they often permit the detection of as little as  $10^{-6}$  or  $10^{-5}$  mg. of an element, or about 1/100 as much as the most sensitive color method as ordinarily carried out, and moreover are more specific than the latter.

Spectrographic detection and determination of elements after chemical enrichment have been applied in a number of cases, but up to the present time chiefly when the direct detection and determination were of low sensitivity. Thus Töpelmann<sup>16</sup> was able to detect  $5 \times 10^{-5}$  per cent of tellurium in bismuth, after precipitation of the tellurium from a 10 g. sample. The direct determination was sensitive to approximately 0.001

<sup>16</sup> H. Töpelmann, *Z. anal. Chem.*, **82**, 284 (1930).

per cent tellurium. Germanium has been concentrated by distillation of the tetrachloride followed by sulfide precipitation;<sup>17</sup> in this way 2  $\gamma$  of germanium could be detected in a 10 g. sample ( $2 \times 10^{-5}$  per cent). Bayle and Amy,<sup>18</sup> isolated minute amounts of various metals by electrolytic deposition on thin wires, and then detected the deposited metal spectrographically. It was possible in this way to detect 0.1  $\gamma$  of copper in 1.5 g. of zinc. Urbain<sup>19</sup> determined minute quantities of gold after electrolytic isolation. The isolation of metals by preliminary electrolysis has also been used by others.<sup>20</sup> Preliminary volatilization of certain elements from a large sample as a means of increasing the sensitivity of their spectrographic determination has already been mentioned (p. 9).

Methods based on fluorescence, and possibly on catalytic activity of the constituent, should be applicable in some cases after enrichment, since they often have high absolute sensitivities. Such methods, however, are inferior to the spectrographic in that they are more subject to interference from foreign elements. When a good method of separation is available which permits a large sample to be worked up, a colorimetric method may be used in the final determination of the isolated constituent. As an illustration we have the determination of selenium in soils, mentioned above, in which distillation provides a simple means of separating the element from very large samples.

## II. Precautions in Trace Analysis

The introduction of foreign substances during the preparation of the sample and in the course of the analysis may have more serious consequences in trace analysis than in any other type of analysis, and special attention must be paid to this source of error.

Great care must be taken to prevent possible gross contamination of the sample through accidental introduction of metal from common articles of the laboratory—iron from ring stands, nickel from crucible tongs, copper and zinc from burners, zinc from rubber, etc. If the sample requires sifting, a silk bolting cloth must be used instead of a metal sieve. The possible introduction of some of the alloying elements of steel must be considered when a Plattner (hardened steel) mortar is used to crush hard materials such as silicates.

Small amounts of certain heavy metals may find their way into the sample from the glass ware and the platinum ware used in the analysis.

<sup>17</sup> W. Geilmann and K. Brünner, *Z. anorg. allgem. Chem.*, **196**, 312 (1931).

<sup>18</sup> E. Bayle and L. Amy, *Bull. soc. chim.* [4], **43**, 604 (1927).

<sup>19</sup> P. Urbain, *Bull. soc. chim.* [4], **47**, 1183 (1930).

<sup>20</sup> A. Schleicher and J. Clermont, *Z. Elektrochem.*, **39**, 2 (1933); A. Schleicher and L. Laurs, *Z. anal. Chem.*, **108**, 241 (1937); A. Schleicher, *ibid.*, **105**, 393 (1936).

Thus Pyrex may yield traces of arsenic, zinc, and lead, and possibly other heavy metals. Platinum ware commonly contains iron, and will nearly certainly yield some of it to acid solutions brought into contact with it. The glaze of porcelain may contain heavy metals such as lead. Fused silica ware is frequently of great value in trace analysis because of its general freedom from heavy metals and its resistance to most acid solutions.

Filter paper always contains small amounts of metals. Thus the following elements have been found in quantitative filter paper:<sup>21</sup> Al, Ba, Ca,

TABLE 2

RETENTION OF IRON, ALUMINUM AND MANGANESE BY SILICA IN ASHING<sup>a</sup>

In each case 5 g. of sample were ashed as indicated; the ash was treated with dilute hydrochloric acid, the solution evaporated to dryness, and the residue extracted with dilute hydrochloric acid; iron, aluminum, and manganese were then determined in the washed residue after hydrofluorization. Samples as follows: No. 1, hay low in silica (0.4% crude SiO<sub>2</sub>), No. 2, hay with normal silica (1.5%), No. 3, straw (2.4% SiO<sub>2</sub>), No. 4, hay high in silica (ca. 4%).

Method of ashing	Sample No.	Amount of metal in silica					
		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>		MnO	
		mg.	% of total	mg.	% of total	mg.	% of total
<i>Over Teclu burner</i>	1	0.61	59	0.42	48	<0.005	< 3
	2	0.30	72	0.54	57	0.03	3.5
	3	0.95	73	1.10	56	0.04	6
	4	1.35	78	2.13	85	0.51	17
<i>In electric muffle furnace</i>	1	0.39	38	0.20	23	<0.005	<3
	2	0.17	40	0.29	30	0.01	1
	3	0.51	39	0.90	45	<0.005	<1
	4	0.98	56	1.59	63	0.09	3

<sup>a</sup> Selection of data from T. Wijkstrom, *Metoder för Undersökning av Fodermedels Mineralbeståndsdelar*. Svanbäck, Stockholm, 1935.

Cr, Cu, Fe, Ge, K, Mg, Mn, Na, Ni, Pb, Sb, Si, Ti, V, Zn, Zr, and the rare earths (especially yttrium). Some of these occur in minute amounts, others in appreciable quantities. For example, Rankama found approximately 1 per cent PbO, 0.3 per cent ZnO, and 0.3 per cent SnO<sub>2</sub> in the ash of quantitative paper; larger amounts of calcium, magnesium, etc., are always present.

Certain volatile substances (*e.g.*, mercury) may be contributed by the atmosphere of the laboratory; they may be absorbed or adsorbed by liquids

<sup>21</sup> K. Rankama, *Bull. comm. géol. Finlande*, No. 126, 14 (1939).

and solids (surfaces of vessels, filter paper, etc.). It hardly needs to be mentioned that care must be taken to exclude dust in the various stages of an analysis.

On the other hand, losses of a trace constituent may sometimes result from interaction with the substance of the containing vessel. For example in ashing samples of organic nature having a low ash content in a silica or porcelain dish, an appreciable fraction of the constituent may be fixed at the surface of the dish, probably by the formation of a silicate which may not be entirely decomposed by acids. The effect is more pronounced when old dishes with rough surfaces are used. The addition of an inert material to diminish surface contact helps to reduce such losses. In the use of platinum vessels at higher temperatures the possibility exists of reduction of a metal compound to metal and the alloying of the latter with the platinum, from which acid will fail to remove it entirely. Loss by adsorption in glass vessels is considered below. Filter paper may adsorb such metals as lead and copper from solutions, especially if these are neutral or only slightly acid; inorganic filter media are in general preferable.

Insoluble material at any stage of a procedure must be regarded with suspicion. The residue may retain heavy metals, sometimes in large quantities. An example of this is afforded by the retention of iron and aluminum, and to a much smaller extent of manganese, by silica in the dry ashing of siliceous organic material (Table 2).

### 1. Reagents

In the determination of the more common heavy metals such as iron, copper, zinc, and lead, for example, it may be necessary to purify the reagents to be used. Special attention must be paid to the distilled water. The ordinary distilled water of the laboratory frequently contains such relatively large amounts of certain metals that its use in trace analysis is out of the question. Water sufficiently pure for most purposes can be obtained by simple redistillation from an all-glass (Pyrex) still.<sup>22</sup> Such water should not contain more than about 1  $\gamma$  lead per liter. It may be stored in Pyrex or other resistant glass.

The common acids of reagent quality are as a rule very low in heavy metals,<sup>23</sup> but when it is necessary to use them in comparatively large quantities (as in the destruction of organic matter in samples of biological

<sup>22</sup> A still with a fused silica condenser is still better but rarely necessary. See J. S. McHargue and E. B. Offutt, *Ind. Eng. Chem., Anal. Ed.*, **12**, 157 (1940), for the description of a still for the production of large volumes of metal-free water (less than 1 part per billion of metal).

<sup>23</sup> It may be mentioned that hydrochloric acid commonly contains appreciable traces of mercury (the chlorine used in the production of hydrogen chloride is obtained by electrolysis of sodium chloride with amalgam electrodes).

origin) they may have to be purified. Distillation in a Pyrex still usually suffices to give a product which is sufficiently pure for nearly all purposes. Perchloric acid may be redistilled under reduced pressure. Hydrofluoric acid may be freed from lead by coprecipitating lead fluoride with strontium fluoride.<sup>24</sup> Pure ammonium hydroxide is most easily obtained by saturating redistilled water in a cooling bath with ammonia from a tank. Ammonium hydroxide is best kept in a ceresin-lined bottle.

Soluble solids may be purified by recrystallization for more or less successful removal of foreign substances in general, or by chemical treatment to remove specific impurities. The latter method is often adopted. A suitable reagent may be added to the solution to form a slightly soluble compound with the substance to be eliminated; it is advisable to use a collector, if possible one that forms mixed crystals with the insoluble body (see further, p. 20). Extraction methods are also useful. For example, a number of heavy metals may be extracted in neutral or slightly basic medium with dithizone (p. 72).

## 2. Blanks

Every analyst knows the necessity for running blanks. A properly run blank takes account of the amounts of constituent contributed by the vessels and by the reagents. The aim in purifying reagents should be to reduce the quantity of the constituent in question to the point where it is small compared to that in the sample; if it is at all feasible the vessels used in the analysis should be of materials that will not yield any appreciable amounts of the constituent to the solutions treated in them. The blank determination should be carried through all the steps of the determination proper. A large blank value is naturally undesirable because it reduces the accuracy of the determination of the constituent in the sample. If it is known or there is good reason to believe that no appreciable amount of the constituent is being contributed by the vessels, it is advisable to run the blank on a larger quantity of reagents than used in the analysis of the sample in order to increase the accuracy.

## 3. Standard Solutions

Dilute solutions of metals used for the preparation of comparison solutions may undergo a serious loss in strength on standing as a result of adsorption or base exchange with the glass container. The loss is greatest

<sup>24</sup> I. T. Rosenqvist, *Am. J. Sci.*, **240**, 358 (1942), adds 10 ml. of 10 per cent strontium chloride per kilogram of the concentrated acid, and repeats the precipitation in the same way. The precipitate is allowed to settle and the supernatant liquid is decanted through a filter in a hard-rubber or paraffined glass funnel. In this way the lead content of acid containing 2 p.p.m. can be reduced to 0.002 p.p.m. or less.

in neutral or slightly basic medium (such as may result from attack of poorly-resistant glass), but may occur as well, but to a smaller extent, in slightly acid solution. Thus Leutwein<sup>25</sup> found that 0.001 per cent solutions of Mo, V, Ti, and Ni showed metal contents 0.2 to 0.4 of the original concentration after storage for 75 days in well-washed Jena glass bottles; 0.001 per cent solutions of Au, Pt, Pd, and Ru decreased to 0.1–0.3 of the original strength after 230 days in Jena glass. In fused silica containers only slight loss in strength was found, except in the case of palladium solution whose concentration decreased to 0.3 of the original after 230 days. According to the writer's experience losses in acid (*ca.* 0.1 *N*) solutions kept in Pyrex are much smaller for most metals than those found by Leutwein, but this source of error is not to be underestimated. It is usually best to prepare the standard solution in two stages. A moderately strong solution (*e.g.*, 0.1 per cent) is prepared in 0.1 to 1 *N* acid. This solution should be stable for a long time, especially if kept in Pyrex, and from it the more dilute standard solution (conveniently 0.001 per cent of metal) may be obtained by dilution. The latter solution should be made slightly acid (0.1 *N* or so if permissible) and stored in Pyrex. It should not show any significant change in the course of a few days or even a week or two.

Standard solutions may be prepared from pure metals or from pure salts of definite composition. If a good grade of "reagent-quality" salt is available it may as a rule be used without further purification for the purposes of colorimetry.<sup>26</sup> Whenever possible anhydrous salts are used. These should be powdered and dried at 100° or higher to remove most of the vacuole water. Hydrated salts may in many instances be used with satisfaction if they are not deliquescent or markedly efflorescent. The crystals should be large enough to permit the picking out of clear uneffloresced individuals. Such air-dry crystals may contain a few parts per thousand of foreign water but this will rarely matter in trace analysis. It is a waste of time to weigh the standard substance too precisely. In preparing a liter of 0.1 per cent solution of hexavalent chromium one should take 3.73 g. of  $K_2CrO_4$ , not 3.734 g.<sup>27</sup>

<sup>25</sup> F. Leutwein, *Zentr. Mineral. Geol.*, 1940A, 129; *Chem. Abstracts*, 34, 5776. For loss of mercury by adsorption see A. Stock, *Ber.*, 72B, 1844 (1939).

<sup>26</sup> Occasionally one runs across directions calling for 2 or 3 recrystallizations of a salt to be used in preparing a standard solution for colorimetry. This gives the impression of an extraordinary degree of impurity for an analytical grade reagent or of an exaggerated opinion of the accuracy of colorimetric methods. The trace analyst may well congratulate himself if the overall accuracy of his determinations corresponds to an error of 1 per cent.

<sup>27</sup> The writer feels compelled to make these self-evident observations on precision because of the seemingly common emphasis on precision where it is meaningless or

#### *4. Sampling*

A relatively large sample is usually taken in colorimetric trace analysis and the obtaining of a representative sample does not as a rule present any special difficulties.<sup>28</sup> The usual precautions should be observed.

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even pernicious. In this connection a flagrant case may be mentioned, in which samples of 50 to 100 g. were weighed to 0.1 mg. although the trace constituent in question could at best be determined no closer than 5 per cent.

<sup>28</sup> An illustration of an exception is afforded by the determination of gold in river waters (Haber) in which the particles consisting of, or carrying, gold are few in number so that 1-2 liter samples may give widely varying results, and an average value is not easily obtained.

## CHAPTER II

### METHODS FOR THE SEPARATION AND ISOLATION OF TRACES OF SUBSTANCES

Few colorimetric reagents are sufficiently specific to allow the determination of an element to be made directly in the presence of associated elements. Whenever possible interfering elements are made harmless by such devices as the adjustment of the  $pH$  of the solution, addition of complex-forming agents, or oxidation or reduction to other valence states, but when such expedients fail recourse must be had to separations. Even when no interfering elements are present it is often necessary, especially when minute amounts of a constituent are being determined, to isolate the element in some way so as to bring it into a small volume of solution.

In this chapter the general methods of separating and isolating trace constituents will be considered. Attention will be confined largely to methods by which quantitative separations can be effected (90 per cent or greater recovery of a *trace* constituent).

#### I. Methods Involving Precipitation, Coprecipitation, Adsorption and Related Processes

These methods all have the following common feature. The solution of the sample is subjected to some process by which two phases result, one a solution containing the macro constituents of the sample, the other a solid phase which is wholly or in part composed of the trace constituent. The general process may be represented as follows:

Solution  $\rightarrow$  solution + solid, where

$C$  = phase containing the macro constituents (and any interfering micro constituents) of the sample,

$c$  = phase containing the micro constituent of the sample that is to be determined.

The processes by which the phase change represented above can be brought about are varied. The simplest one is a precipitation of the trace constituent, which leaves the macro constituents in solution. However, precipitation in its simple form is usually not applied when a trace constituent is present in very low concentration. Even if the precipitate has a very low solubility its separation may involve difficulties when the absolute amount is small. A colloidal suspension may be formed, or the solution may become supersaturated without precipitation occurring, etc. Therefore, a small amount of another substance forming a slightly soluble product



with the precipitant is added to the solution. The precipitate produced from the added substance is called the *collector*, a term which describes its function rather well.

Sometimes the collector functions in a more or less mechanical way. Thus, when aluminum is added to a solution of quadrivalent titanium so dilute that a reaction can not be obtained even with thymol (p. 424) and precipitated with ammonium hydroxide, the aluminum hydroxide carries down the titanium hydroxide by entrainment, and titanium can be determined colorimetrically in the precipitate after it has been dissolved. In this way amounts of titanium of the order of 1 microgram per liter can be determined.<sup>1</sup>

Collectors are frequently used in the precipitation of sulfides. Copper sulfide has been employed as a collector for molybdenum,<sup>2</sup> zinc,<sup>3</sup> lead<sup>4</sup> and other metals; lead sulfide has been used for copper,<sup>5</sup> silver sulfide for lead,<sup>6</sup> etc. In many cases the sulfide collector functions largely in a mechanical or physical manner, but in others there is an additional effect due to operation of processes which are included in the term coprecipitation.<sup>7</sup> For example, there may be mixed crystal formation between the collector and the trace precipitate. Also the collector may promote the precipitation of the micro constituent from its supersaturated solution.<sup>8</sup>

The completeness of separation of a particular metal by sulfide precipitation naturally depends to a large extent upon the solubility of its sulfide, especially if the collector does not form mixed crystals with the latter. As little as 0.02  $\gamma$  of mercury can be isolated from a liter of solution by hydrogen sulfide precipitation (copper sulfide as collector).<sup>9</sup> On the other hand, lead sulfide, which has a solubility product equal to  $3.4 \times 10^{-28}$ , much greater than that of mercuric sulfide, may not be quantitatively precipitated from an acid solution, even if a collector such as silver sulfide is used (lead and silver sulfides are not isomorphous). It may be calculated that the solubility of lead sulfide in a 1 *N* acid solution saturated with hydrogen sulfide is  $3 \times 10^{-5}$  M, which corresponds to about 6 mg. Pb per liter. In 0.1 *N* acid, saturated with hydrogen sulfide, the calculated solubility corresponds to 0.06 mg. Pb per liter, which is still a rather large

<sup>1</sup> V. T. Chufko, *Zavodskaya Lab.*, **8**, 950 (1939).

<sup>2</sup> G. von Hevesy and R. Hobbie, *Z. anorg. allgem. Chem.*, **214**, 380 (1933).

<sup>3</sup> R. E. Lutz, *J. Ind. Hyg. Toxicol.*, **7**, 273 (1925).

<sup>4</sup> R. L. Lucas and F. Grassner, *Mikrochemie (Emich Festschrift)*, **1930**, p. 203.

<sup>5</sup> R. Lucas and F. Grassner, *Mikrochemie (Emich Festschrift)*, **1930**, p. 199.

<sup>6</sup> G. von Hevesy and R. Hobbie, *Z. anal. Chem.*, **88**, 1 (1932).

<sup>7</sup> I. M. Kolthoff, *J. Phys. Chem.*, **36**, 860 (1932); *Chem. Weekblad*, **31**, 102, 230 (1934).

<sup>8</sup> Cf. in this connection, I. M. Kolthoff and E. Pearson, *J. Phys. Chem.*, **36**, 549 (1932).

<sup>9</sup> A. Stock, F. Cucuel, and H. Köhle, *Z. angew. Chem.*, **46**, 187 (1933).

value from the viewpoint of the trace analyst. Actually the solubility may be greater than the calculations indicate because equilibrium in a metal-hydrogen sulfide system is attained with notorious slowness. One of the functions of a collector is to hasten the attainment of equilibrium. Nevertheless, it is advisable in precipitation of traces of sulfides to let the solution stand overnight before filtration.<sup>10</sup> Moreover, the acidity of the solution should be no higher than necessary to keep other metals in solution.

Occasionally a slightly soluble metal-organic complex is used to carry down traces of other metals forming insoluble compounds with the same reagent. Traces of zirconium, vanadium, and titanium occurring in mineral waters can be quantitatively recovered by collection in a precipitate of iron cupferrate produced by the addition of cupferron.<sup>11</sup> 8-Hydroxyquinoline has also been used to precipitate traces of various metals with ferric or aluminum quinolate as the gathering agent (*cf.* p. 200).

If the collector forms mixed crystals with the corresponding compound of the trace constituent, the precipitation of the latter may be virtually complete even though the same compound of the trace constituent alone in solution might not precipitate at all. This may be illustrated by the system lead sulfate-strontium sulfate, the components of which are isomorphous and form mixed crystals. If an excess of sulfate is added to a solution containing strontium ions and a trace of lead ions, practically all of the latter are removed from solution by incorporation in the strontium sulfate precipitate, the following relation holding approximately:

$$\frac{[\text{Pb}^{++}]_{\text{crystals}}}{[\text{Pb}^{++}]_{\text{solution}}} = K \frac{[\text{Sr}^{++}]_{\text{crystals}}}{[\text{Sr}^{++}]_{\text{solution}}}$$

The distribution coefficient,  $K$ , ideally is equal to the ratio of the solubility products of the two components,

$$\frac{S_{\text{SrSO}_4}}{S_{\text{PbSO}_4}} = \frac{3 \times 10^{-7}}{10^{-8}} = 30$$

The expression for the distribution of lead between precipitate and solution holds for equilibrium conditions; in the rapid formation of precipitate the relation is no longer fulfilled, and, moreover, the value of  $K$  is usually not very close to the calculated value.<sup>12</sup> These deviations, however, do not destroy the general usefulness of the equation for calculating the approximate amount of lead in the precipitate. It is not difficult to arrange matters so that 99 per cent of the added strontium is precipitated,

<sup>10</sup> In this connection, see p. 214.

<sup>11</sup> L. W. Strock and S. Drexler, *J. Optical Soc. Am.*, **31**, 167 (1941).

<sup>12</sup> *Cf.* the system lead sulfate-barium sulfate, I. M. Kolthoff and G. Noponen, *J. Am. Chem. Soc.*, **60**, 197 (1938).

and therefore lead must be strongly concentrated in the precipitate, even if  $K$  had a value of 1. Hahn<sup>13</sup> has shown that when 50 per cent of the strontium in a solution is precipitated as the sulfate, approximately 99 per cent of the total lead (as the isotope Th B) originally in the solution is found in the precipitate.

The lead in the strontium sulfate precipitate can be recovered by converting the sulfates to carbonates and dissolving the latter in acid. The isolation of lead by coprecipitation with strontium or barium sulfate is usually of slight practical importance in colorimetric trace analysis, because it is usually more advantageous to separate traces by extraction with dithizone in an organic solvent (p. 279).<sup>14</sup>

Foreign substances may have a marked effect on the separation of traces by mixed-crystal formation. For example, chloride has an inimical effect on the coprecipitation of lead with strontium sulfate. Thus, in a 1  $N$  potassium chloride solution, 82 per cent of the lead is found in the precipitate when 50 per cent of the strontium is precipitated, and only 30 per cent of the lead is carried down when the precipitation is made in 2.5  $N$  potassium chloride solution. The unfavorable effect of chloride may be attributed to the formation of a complex lead chloride which is not incorporated in the strontium sulfate lattice.<sup>13</sup> Arsenic (V) can be coprecipitated with magnesium ammonium phosphate<sup>15</sup> and vanadium (V) with ammonium phosphomolybdate.<sup>16</sup> These are cases of mixed crystal formation.

The phenomenon of anomalous mixed crystal formation<sup>17</sup> may find application in the separation of traces of metals. For example, lead is enriched in alkali halides crystallizing from aqueous solution. When 18.4 per cent of potassium chloride in a solution is crystallized out, 92.8 per cent of the lead (as Th B) in the solution is incorporated in the crys-

<sup>13</sup> O. Hahn, *Applied Radiochemistry*. Cornell Univ. Press, Ithaca, 1936; p. 105.

<sup>14</sup> J. T. Rosenqvist, *Am. J. Sci.*, **240**, 356 (1942), has employed coprecipitation of lead sulfate with strontium sulfate for the isolation of lead in silicate rocks. He used samples of 50–300 g. and finally weighed the lead as the dioxide after electrolytic deposition. The object of this work was not only the determination of the percentage of lead, but also the separation of enough of the element to enable its isotopic composition to be determined.

<sup>15</sup> I. M. Kolthoff and C. W. Carr, *J. Phys. Chem.*, **47**, 148 (1943).

<sup>16</sup> J. R. Cain and J. C. Hostetter, *J. Ind. Eng. Chem.*, **4**, 250 (1912); *J. Am. Chem. Soc.*, **43**, 2552 (1921).

<sup>17</sup> When on chemical and crystallographic grounds no mixed crystal formation between two components is to be expected and yet, in spite of the non-fulfillment of the conditions of isomorphism, solid solutions apparently identical with mixed crystals are formed by them, the term *anomalous mixed crystal* formation is applied to the phenomenon. See O. Hahn, *Applied Radiochemistry*,<sup>13</sup> p. 98.

tals,<sup>18</sup> the partition coefficient having the value 57. This example is a warning against the assumption often tacitly made that recrystallization of an easily soluble salt gives a product of greater purity.

Compound formation is sometimes involved in the carrying down of a trace constituent by a collector. Thus ferric hydroxide readily carries down arsenic (III and V) and phosphorus, slightly soluble ferric arsenite, arsenate, and phosphate being formed. The precipitation of the micro constituent may be more complete than would be expected from the solubility of the compound formed, because there is strong adsorption of ferric arsenate, for example, from its saturated solution by ferric hydroxide. Another case of compound formation in precipitation is encountered in the use of tellurium as a collector for gold, platinum,<sup>19</sup> and palladium. These metals are quantitatively carried down when a reducing agent such as sulfurous acid or stannous chloride is added to a solution containing them and a small amount of an alkali tellurite. It seems likely that the noble metals form tellurides under these conditions and are precipitated as such with the reduced tellurium. However, the precipitation of these metals would doubtless be just as complete if no compound formation occurred and they acted simply as crystallization centers for the elemental tellurium. The latter type of collection of a trace element is illustrated by the addition of an alkali stannite solution to a solution containing lead ions and a trace of bismuth. The reduced bismuth forms nuclei on which lead is speedily deposited; in the absence of bismuth the reduction of lead by stannite is very slow.<sup>20</sup> This particular case is of no great practical importance from the quantitative standpoint but analogous cases may find application.

The choice of a collector is governed by a number of factors, of which the first is naturally its ability to carry down the trace substance with sufficient completeness for the purpose. A good collector is one that will catch the trace element completely even when used in small amount. Limitation of the amount of collector is often of importance, since other substances in solution may be coprecipitated with it to a greater or less extent, and later lead to interference in the determination. An efficient collector can be used in minimum quantities and the coprecipitation of undesired constituents thus reduced in absolute amount to the point where they will do no harm. Preference is of course given to a collector which is more or less specific in its action, but this is a desideratum which is rarely entirely satisfied. Collectors functioning by mixed crystal formation are the most

<sup>18</sup> O. Hahn, *Applied Radiochemistry*. Cornell Univ. Press, 1936; p. 103.

<sup>19</sup> S. K. Hagen, *Mikrochemie*, **20**, 180 (1936).

<sup>20</sup> F. Feigl, *Specific and Special Reactions*. Nordeman, New York, 1940; p. 75.

satisfactory in this respect. The collector should be a substance which does not interfere in the final determination of the micro constituent. If this condition cannot be fulfilled the collector should be easily volatile so that it can be eliminated after it has served its purpose. In this respect

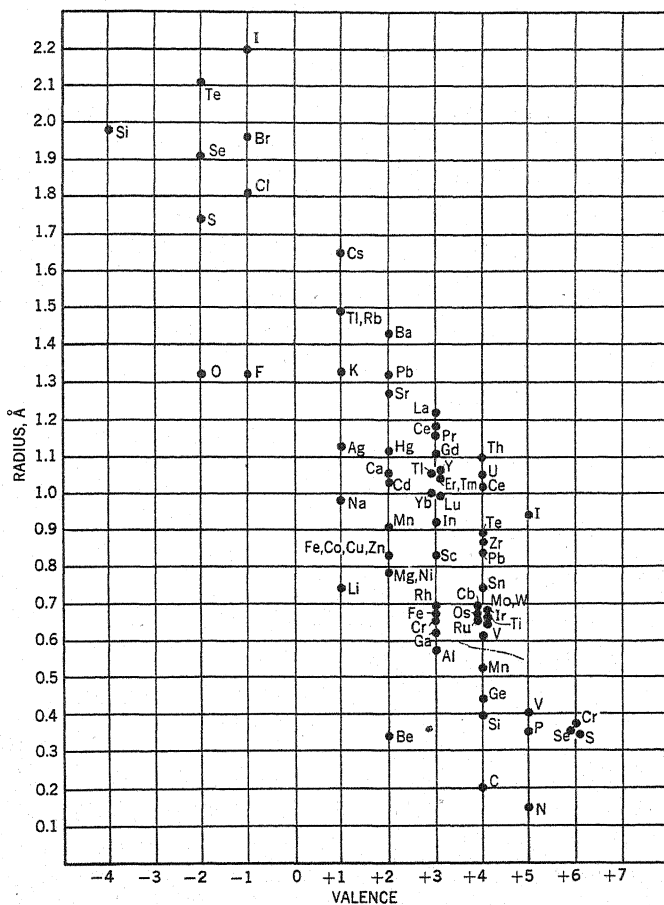


Fig. 2.—Empirical ionic radii. (According to V. M. Goldschmidt.)

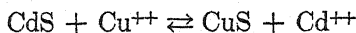
mercuric and arsenic sulfides have advantages for collecting heavy metal sulfides, and the same is true for tellurium used to gather the precious metals.

As a guide in choosing collectors for coprecipitation by mixed crystal formation, ionic radii of the elements are given in Fig. 2.

### 1. *Precipitation or Adsorption by a Solid*

It is sometimes advantageous to use a slightly soluble solid as a precipitant or as an adsorbant for a trace constituent in solution. One cannot always distinguish the two effects sharply; in either case the solid acts as a collector.

Clarke and Hermance<sup>21</sup> have shown that paper which has been impregnated with a slightly soluble solid may be used in isolating minute amounts of metal in large volumes of solution. For example, by passing a solution containing copper in very low concentration through a disk of filter paper impregnated with cadmium sulfide, copper is precipitated on the paper according to the reaction:



The solubility product of CuS,  $9 \times 10^{-45}$ , is so much smaller than that of CdS,  $4 \times 10^{-29}$ , that the above reaction can be made to run to practical completion from left to right under proper conditions of acidity and rate of flow. If necessary a number of impregnated disks can be used in series. In this way from 90 to 100 per cent of 20 to 50  $\gamma$  of copper present in 500 ml. of a solution 0.01 *M* in sulfuric acid and 0.1 *M* in sodium acetate could be recovered. The paper disks can be ashed and the copper or other precipitated metal determined by any suitable colorimetric method, or the spot can be compared with standard spots obtained in a similar manner, after dissolving out the cadmium sulfide by immersion in warm 1 *M* hydrochloric acid. The method may be used to separate as little as 0.0001 per cent of copper from nickel, and also copper from lead. By the use of a zinc sulfide impregnated paper, traces of lead can be removed from a neutral solution.

Extremely minute amounts of gold, platinum, palladium, selenium, tellurium, and arsenic can be removed from acid solution by shaking the solution with mercurous chloride.<sup>22</sup> These metals are reduced to the elemental condition on the surface of the mercurous chloride and impart a strong color to it (p. 256).

Lead is strongly adsorbed on calcium carbonate, and can in this way be isolated from tap water. The strong adsorption is explained by the slight solubility of lead carbonate. It may also be mentioned that lead can be removed from water by filtration through a wad of cotton.<sup>23</sup> This method is of little practical importance for separating small amounts of lead, but this example of the strong adsorptive properties of cellulose serves as a warning against the inherent danger of partial or complete loss of a trace

<sup>21</sup> B. L. Clarke and H. W. Hermance, *Ind. Eng. Chem., Anal. Ed.*, **10**, 591 (1938); **9**, 292 (1937).

<sup>22</sup> G. G. Pierson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 437 (1934).

<sup>23</sup> G. Frerichs, *Apoth. Ztg.*, **17**, 884 (1902).

constituent when a solution is filtered through paper under some conditions.

The above examples indicate that a pre-formed, slightly soluble substance may be used effectively in a number of cases to separate a trace constituent. As a general rule, however, the separation is more complete and certain, or at least more rapid, if the solid phase is formed in the solution containing the trace constituent. Thus if the main concern of an analyst is to isolate a trace of gold from solution he would prefer to precipitate mercurous chloride in the solution rather than to shake the solution with added mercurous chloride. In the former case a greater effective surface of the mercurous chloride is available for the incorporation of gold in the precipitate and moreover the coprecipitation is more rapid than the adsorption. If it is desired, however, to determine gold in a solution by surface coloration on mercurous chloride the solid would of course be added pre-formed.

## 2. Chromatographic Separations

Preferential adsorption of cations and anions on aluminum oxide by the chromatographic technique offers a possible method of separation or enrichment of inorganic trace constituents.<sup>24</sup> For example, ferric iron can be detected at a concentration of  $10^{-4}$  M in 1 M cobalt or copper solutions, and 1  $\gamma$  of copper can be detected in a molar solution of cobalt or cadmium.<sup>25</sup>

## 3. Zeolitic Exchange

The use of zeolites in the concentration of metal traces offers promise. Little work has been done in this direction. Abrahamczik<sup>26</sup> has shown that by permutit exchange minute amounts of iron can be isolated and determined. Ten liters of distilled water containing 0.0025 part per million of ferrous iron were run through a  $50 \times 450$  mm. column of "neopermutite" (about 400 g.). One hundred ml. of warm saturated sodium chloride solution were then passed slowly through the column in the reverse direction, followed by 150 ml. of wash water. Iron was determined colorimetrically in an aliquot of the combined solutions, and 90 per cent of that added was found.

## 4. Electrolysis

The isolation of traces of metals from large volumes of solution may frequently be effected by electrolytic deposition. Among the metals

<sup>24</sup> Regarding inorganic chromatography see G.-M. Schwab and K. Jockers, *Angew. Chem.*, **50**, 546 (1937); G.-M. Schwab and G. Dattler, *ibid.*, **50**, 691 (1937); **51**, 701 (1938). For the use of oxine in inorganic chromatography see H. Erlenmeyer and H. Dahn, *Helv. Chim. Acta*, **22**, 1369 (1939).

<sup>25</sup> G.-M. Schwab and K. Jockers.<sup>24</sup>

<sup>26</sup> E. Abrahamczik, *Mikrochemie*, **25**, 230 (1938).

which have been isolated in this manner are copper,<sup>27</sup> lead,<sup>28</sup> mercury,<sup>29</sup> zinc, silver, and gold (cf. p. 281).

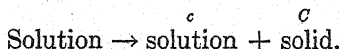
The electrolytic separation of mercury has proven of great value in the determination of minute amounts of the element in connection with studies of mercury poisoning.

Von Hevesy and Hobbie<sup>30</sup> made use of the electrolytic deposition of lead as the dioxide in the determination of the metal in silicate rocks. The deposited oxide was determined colorimetrically with tetramethyldiamidodiphenylmethane. The recovery of lead, however, was not quantitative and the true value had to be found by a radiometric method.

A special apparatus for the deposition of traces of metals from large volumes of solution has been described by Clarke and Hermance.<sup>31</sup> These authors worked with solutions having a volume of 250 ml. containing 5 or 10 g. of metal in which the trace constituent was to be determined. The deposited metal was determined gravimetrically or volumetrically, and it was possible to determine as little as 0.1 mg. of zinc in 5 g. of aluminum with an accuracy of 1 per cent, 0.1 mg. of lead in 10 g. of zinc with an accuracy of 4 per cent, and 0.1 mg. of copper in 5 g. of nickel with an accuracy of 3 per cent. There seems to be no reason why the weight of sample used cannot be much reduced and the deposited metal determined by a suitable colorimetric method instead of gravimetrically or volumetrically.

#### 5. Separations in which the Trace Constituent Is Left in Solution and the Macro Constituents Are Precipitated

This case is represented by:



In general it may be said that this method should be avoided so far as possible in trace analysis. In the first place, the precipitation of a large amount of substance involves the danger of greater or less loss of the trace constituent as a result of coprecipitation, and it must always be regarded with suspicion. If the coprecipitation is not extensive, a reprecipitation may result in a satisfactory separation. Each particular system of  $c$  and  $C$  must be tested. Even if a satisfactory separation can be effected in this way, the trace constituent is usually left in a large volume of solution and

<sup>27</sup> R. Lucas and F. Grassner, *Mikrochemie (Emich Festschrift)*, 1930, p. 199.

<sup>28</sup> R. Lucas and F. Grassner, *Mikrochemie (Emich Festschrift)*, 1930, p. 201.

<sup>29</sup> See especially A. Stock, *Ber.*, 71, 550 (1938).

<sup>30</sup> G. von Hevesy and R. Hobbie, *Z. anal. Chem.*, 88, 1 (1932).

<sup>31</sup> B. L. Clarke and H. W. Hermance, *J. Am. Chem. Soc.*, 54, 877 (1932).



its subsequent determination may first require its isolation or concentration from this solution. Sometimes this method of separation must be applied for the lack of a better one.<sup>32</sup>

An exception to the statements made in the preceding paragraph is found in the use of electrolysis for separation of the major constituents. The electrolysis is usually carried out with a mercury cathode, so that this case does not strictly come under the above heading (see p. 124). In dilute sulfuric acid solution many metals such as iron, chromium, nickel, cobalt, zinc, cadmium, gallium, copper, tin, molybdenum, bismuth and silver are deposited in the mercury, while such elements as aluminum, titanium, zirconium, phosphorus, vanadium, and uranium are quantitatively left in solution.<sup>33</sup> The method is chiefly valuable in the determination of the latter elements in metallurgical materials. Thus electrolysis with a mercury cathode provides an excellent method for the separation of interfering iron in a determination of aluminum in steel.

## II. Extraction by an Immiscible Solvent

$\overset{c}{\text{Solution 1}} \rightarrow \text{solution 1} + \overset{c}{\text{solution 2}}$

Extraction of a trace constituent from an aqueous solution by an immiscible organic solvent is frequently the ideal method of separating it from large amounts of foreign substances. The process is often very selective, and the isolation of the substance can be made as complete as desired in most cases by repetition of the extraction. Even when a separation from other substances is not involved, an extraction method can be of great value in isolating a minute amount of constituent from a large volume of aqueous solution and concentrating it in a small volume of an immiscible solvent, thus making the determination highly sensitive when the extracted compound is colored.

Occasionally inorganic compounds can be extracted as such (ferric chloride, auric chloride and other metal chlorides by ether (see p. 249), osmium tetroxide by carbon tetrachloride, etc.) but usually in the case of metals one adds an organic reagent forming an internal complex salt<sup>34</sup>

<sup>32</sup> In this connection it may be mentioned that sometimes small amounts of an interfering constituent that cannot be completely precipitated can be removed by coprecipitation. Thus scandium hydroxide is not completely precipitated by sodium hydroxide, but if a small amount of cobalt is present it is completely carried down in the cobalt hydroxide precipitate.

<sup>33</sup> W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*. Wiley, New York, 1929; p. 105; G. E. F. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis*. Wiley, New York, 1931; p. 94.

<sup>34</sup> For a discussion of inner complex compounds see F. Feigl, *Specific and Special Reactions*. Nordeman, New York, 1940; p. 35.

which is often extractable by various organic solvents, the partition coefficient frequently being very favorable. Organic reagents are valuable in extraction procedures not only because they may be highly selective, but also because the metal-complex formed may be colored, so that a metal can sometimes be separated and determined in one operation, as is illustrated by the use of diphenylthiocarbazone.

Extraction methods are of wide applicability, and there are few metals, with the exception of the alkalis and alkaline earths, which cannot be extracted as the internal complex salt of some organic reagent. The outstanding reagent for extraction separation of metals is diphenylthiocarbazone (dithizone) which is treated at length in Chapter III, p. 72. Other reagents which give metal compounds extractable by organic solvents include cupferron (for iron and other metals), 8-hydroxyquinoline (for aluminum, iron, gallium, vanadium, etc.), sodium diethyldithiocarbamate (for copper, lead, zinc, etc.), potassium xanthate (for arsenic), dimethylglyoxime (for nickel), and  $\alpha$ -nitroso- $\beta$ -naphthol (for cobalt, copper, etc.).

The distribution ratio of an extractable substance is independent of its initial concentration in a given aqueous solution, provided the molecular weight of the partitioning substance is the same in both phases, and no other complicating factors enter in. Thus Grahame and Seaborg<sup>35</sup> found that the distribution ratio of gallium chloride between ether and 6 *N* hydrochloric acid was the same within the experimental error whether the gallium concentration was  $10^{-12}$  *M* (radio-active isotope of gallium) or 0.0016 *M*, being 17.5–18.1 in the first case and 16.9 in the second. Likewise the distribution of  $(\text{NH}_4)_2\text{Co}(\text{CNS})_4$  between amyl alcohol and an aqueous solution was found to be the same whether the initial concentration of cobalt was  $10^{-12}$  *M* or  $10^{-5}$  *M*.

Ferric chloride and gold (III) chloride show an anomalous behaviour when extracted from an aqueous hydrochloric acid solution by ethyl or isopropyl ether. The lower the concentration of ferric iron the smaller is the percentage of iron extracted by the ether. This is illustrated by Fig. 3 which gives the percentage of iron extracted by isopropyl ether from solutions of various concentrations in 5 *N* hydrochloric acid. At higher hydrochloric acid concentrations the extraction of iron is much more complete. Thus at an acid concentration of 7.5 and 8.0 *M* (the optimum), 96 per cent of the iron in 25 ml. of aqueous solution containing 1 mg. can be extracted with an equal volume of isopropyl ether<sup>36</sup>. This example shows it is not always safe to assume that a substance will be extracted as easily at low concentrations as at higher ones.

In nearly all extractions the acidity of the aqueous phase plays an im-

<sup>35</sup> D. C. Grahame and G. T. Seaborg, *J. Am. Chem. Soc.*, **60**, 2524 (1938).

<sup>36</sup> R. W. Dodson, G. J. Forney, and E. H. Swift, *J. Am. Chem. Soc.*, **58**, 2575 (1936).

portant role, and there is generally an acidity range in which the extraction reaches a maximum. With certain organic reagents such as oxine and dithizone various separations of metals become possible by the adjustment of the  $pH$ .

The effect of foreign substances on the extraction or non-extraction of a substance is relatively slight as a rule if these do not alter the  $pH$  of the medium or react chemically with the given substance. An interesting example has been given by Grahame and Seaborg,<sup>37</sup> who found that on shaking a hydrochloric acid solution containing ferric chloride and cobalt chloride (as the radioactive isotope) in the ratio  $10^8:1$  with ether, the iron was nearly completely removed but no cobalt passed into the ether. The

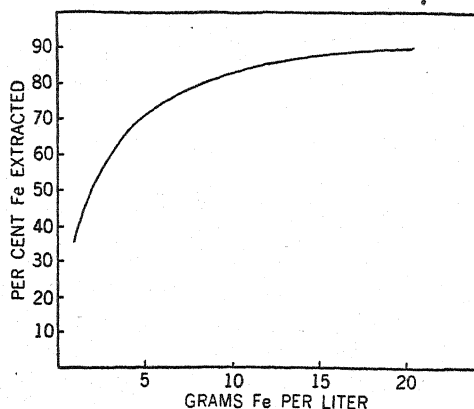


Fig. 3.—Extraction of ferric chloride by isopropyl ether from 5.0  $N$  hydrochloric acid at various iron concentrations (volume of each phase originally equal). (From data of Dodson, Forney and Swift.)

distribution ratio of cobalt chloride between ether and 5.5  $N$  hydrochloric acid is of the order of 0.0001 at  $20^\circ$ , and is not significantly altered by the presence of ferric iron. This example is an illustration of the possibility of removing an interfering macro constituent from a solution by extraction in a case in which separation by precipitation would lead to serious loss of the micro constituent.

An example of increase in the extractability of a substance by another is afforded by the effect of ferric iron on phosphoric acid. The latter is hardly extracted at all from a hydrochloric acid solution by isopropyl ether when present alone, but if ferric iron is also present more than one-half of the phosphoric acid may be extracted under certain conditions, presumably because of the formation of a complex ferric phosphoric acid.

<sup>37</sup> D. C. Grahame and G. T. Seaborg, *J. Am. Chem. Soc.*, **60**, 2527 (1938).

On the other hand an extraneous substance may reduce or prevent the extractability of another substance by chemical reaction (reaction of fluoride with ferric iron to give complex fluoride, or reduction of ferric iron to ferrous).

### 1. *Dry or Fire Assaying*

This is a high temperature extraction process which is of great importance in the isolation of gold, silver, and the platinum metals. A mixture of the sample, lead oxide, flux and reducing agent is heated to a high temperature. The precious metals present dissolve in the molten lead which sinks to the bottom of the crucible. The lead is removed by cupellation, the molten lead oxide being absorbed by the cupel, while the precious metal globule is not, and after appropriate treatment to remove silver, the bead of gold can be weighed or its diameter measured microscopically.

### 2. *Extraction of Solid Mixtures*

Another type of extraction process of lesser importance that may be considered here for convenience involves treatment of a solid mixture with a solvent (usually organic) which will dissolve the compound of the trace constituent but not the compounds of the macro constituents to any appreciable extent. This process finds occasional application in trace analysis. For example, lithium chloride may be dissolved out of a mixture of the other alkali metal chlorides by various organic solvents. In such a process there is danger that the large amount of insoluble material will occlude some of the soluble and prevent its complete extraction. For this reason it may be preferable to use a precipitation process instead. Thus in the Palkin method for the separation of lithium, the solution of the alkali chlorides in as small a volume of water as possible is poured into a mixture of absolute alcohol and ether; sodium and potassium chlorides are precipitated and lithium chloride remains in solution.<sup>33</sup>

The reverse application of extraction of solid mixtures—dissolving the compounds of the macro constituents and leaving the compound of the micro constituent undissolved—must be regarded as a dubious procedure because of the great effect of solubility loss even if the absolute solubility of the micro compound is extremely small. The isolation of very small amounts of sodium chloride occurring in lithium chloride by solution of the latter in an anhydrous organic solvent can hardly be considered a feasible procedure.

<sup>33</sup> S. Palkin, *J. Am. Chem. Soc.*, **38**, 2326 (1916).

TABLE 3  
VOLATILIZATION OF METALLIC COMPOUNDS FROM PERCHLORIC AND SULFURIC ACID  
SOLUTIONS AT 200-220 °<sup>a</sup>

*Procedure 1* ( $\text{HClO}_4\text{-HCl}$ ): 15 ml. of 60%  $\text{HClO}_4$  added to metal chloride or perchlorate solution in a Scherrer distilling flask. Distillation made in a stream of  $\text{CO}_2$ . Temperature raised to 200°, and hydrochloric acid then added at such a rate that temperature remained at 200-220°. Distillation stopped after 15 ml.  $\text{HCl}$  had been added over a period of 20-30 minutes.

*Procedure 2* ( $\text{HClO}_4\text{-HBr}$ ): As in (1) except 40%  $\text{HBr}$  used in place of  $\text{HCl}$ .

*Procedure 3* ( $\text{HClO}_4\text{-H}_3\text{PO}_4\text{-HCl}$ ): As in (1) except 5 ml. 85%  $\text{H}_3\text{PO}_4$  added to flask before distillation.

*Procedure 4* ( $\text{HClO}_4\text{-H}_3\text{PO}_4\text{-HBr}$ ): As in (3) except  $\text{HCl}$  substituted for  $\text{HBr}$ .

*Procedure 5* ( $\text{H}_2\text{SO}_4\text{-HCl}$ ): As in (1) except  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) substituted for  $\text{HClO}_4$ .

*Procedure 6* ( $\text{H}_2\text{SO}_4\text{-HBr}$ ): As in (2) except  $\text{H}_2\text{SO}_4$  substituted for  $\text{HClO}_4$ .

Approximate Percentage of Element Volatilized from 20-100 mg.  
Portions by Distillation with:

Element	$\text{HCl-HClO}_4$ Proc. 1	$\text{HBr-HClO}_4$ Proc. 2	$\text{HCl-H}_3\text{PO}_4\text{-HClO}_4$ Proc. 3	$\text{HBr-H}_3\text{PO}_4\text{-HClO}_4$ Proc. 4	$\text{HCl-H}_2\text{SO}_4$ Proc. 5	$\text{HBr-H}_2\text{SO}_4$ Proc. 6
As(III)	30	100	30	100	100	100
As(V)	5	100	5	100	5	100
Au	1	0.5	0.5	0.5	0.5	0.5
B	20	20	10	10	50	10
Bi	0.1	1	0	1	0	1
Cr(III)	99.7	40	99.8	40	0	0
Ge <sup>b</sup>	50	70	10	90	90	95
Hg(I)	75	75	75	75	75	90
Hg(II)	75	75	75	75	75	90
Mn	0.1	0.02	0.02	0.02	0.02	0.02
Mo	3	12	0	0	5	4
Os <sup>c</sup>	100	100	100	100	0	0
P	1	1	1	1	1	1
Re	100	100	80	100	90	100
Ru	99.5	100	100	100	0	0
Sb(III)	2	99.8	2	99.8	33	99.8
Sb(V)	2	99.8	0	99.8	2	98
Se(IV)	4	2-5	2-5	2-5	30	100
Se(VI)	4	5	5	5	20	100
Sn(II)	99.8	100	0	99.8	1	100
Sn(IV)	100	100	0	100	30	100
Te(IV)	0.5	0.5	0.1	0.5	0.1	10
Te(VI)	0.1	0.5	0.1	1	0.1	10
Tl <sup>d</sup>	1	1	1	1	1	1
V	0.5	2	0	0	0	0

The following elements are not volatilized in any of the procedures: Ag, alkalis (Li, Na, K, Rb, Cs), Al, Ba, Be, Ca, Cb, Cd, Co, Cu, Fe, Ga, Hf, In, Ir, Mg, Ni, Pb, Pd, Pt, rare earths, Rh, Si, Ta, Th, Ti, U, W, Zn, Zr.

<sup>a</sup> J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **22**, 465 (1939).

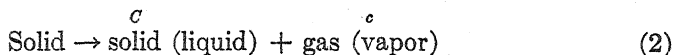
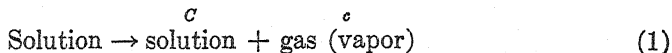
<sup>b</sup>  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  solutions heated to 200° before admitting  $\text{HCl}$  or  $\text{HBr}$ .

<sup>c</sup> At 200-220°, no  $\text{Os}$  is volatilized from  $\text{H}_2\text{SO}_4$ , but at 270-300° it is completely volatilized.

<sup>d</sup> No  $\text{Tl}$  distills if it is univalent (reduction with  $\text{SO}_2$ ).

### III. Methods Involving Evolution of a Gas, Distillation and Volatilization

These processes are based on the following transformations:



The process represented by (1) is of more general applicability than that represented by (2). The former process involves evolution of a gas and distillation, and the latter volatilization. All of the non-metallic elements can be transformed into compounds which can be separated as a gas or vapor. A considerable number of the metals and metalloids, including germanium, arsenic, selenium, tin, antimony, ruthenium, osmium and rhenium, can be separated by distillation from aqueous solution after conversion into suitable compounds (Table 3). Less often, in the case of metals, evolution methods find application, as for instance in the evolution of arsenic as arsine. Mercury as the metal or as a compound can of course be volatilized easily by heating a solid sample and this method has been applied in the isolation of extremely small amounts occurring in rocks.

Very sharp separations are often possible by the use of evolution, distillation, and volatilization methods. As a rule large amounts of foreign material do not hinder the separation of traces by these processes, and consequently methods based on them give admirable results, which sometimes could not be obtained at all by other methods.

The converse process, in which one or more major constituents are volatilized, is illustrated by the use of hydrofluoric acid in the decomposition of silicates which leads to the expulsion of  $\text{SiF}_4$ , thus eliminating a constituent that could not readily be removed in any other way. Tin, in tin alloys, can be volatilized by evaporation of the sample with a mixture of bromine and hydrobromic acid.

### CHAPTER III

## COLORIMETRY AND SPECTROPHOTOMETRY IN TRACE ANALYSIS

The wide use of colorimetric and spectrophotometric methods in analytical chemistry is based on the possibility of converting the constituent to be determined into a substance whose solution (or suspension) is strongly colored. Such a solution shows differential absorption of light of different wave lengths. When the percentage of light transmitted by the solution is plotted against the wave length, a *transmission curve* is obtained, which in most cases shows one or two maxima or minima, but which sometimes may be more complex (Figs. 4 and 5). Instead of plotting the transmittancy against the wave length, the percentage of light absorbed may be plotted and an *absorption curve* is then obtained.

In the great majority of cases in which dilute solutions are involved, the following relation (which can be derived *a priori*) between the intensity of the incident and the transmitted monochromatic light (Figure 6) in terms of the concentration of the colored substance in the solution and the depth of the solution is found to hold closely:

$$I/I_0 = 10^{-kcl}, \quad (1)$$

in which  $I_0$  = intensity of the incident light beam,

$I$  = intensity of the transmitted light beam,

$k$  = a constant (specific extinction) whose value for specified units depends upon the solvent and the temperature as well as upon the wave length of the light,

$c$  = concentration of the colored substance,

$l$  = depth of solution traversed by the light.

This relation is generally known as the law of Lambert-Beer or Bouguer-Beer.<sup>1</sup>

If the concentration is expressed in moles per liter and the depth in centimeters,  $k$  becomes the *molar or the molecular extinction coefficient*, usually designated  $\epsilon$ .

Equation (1) may be written:

$$\begin{aligned} \log_{10} I/I_0 &= -kcl \\ \text{or} \quad \log_{10} I_0/I &= kcl \end{aligned} \quad (2)$$

<sup>1</sup> The law of Beer gives the relation between  $I$  and  $I_0$  at constant depth and variable concentration, that of Lambert the relation between  $I$  and  $I_0$  at constant concentration and variable depth.

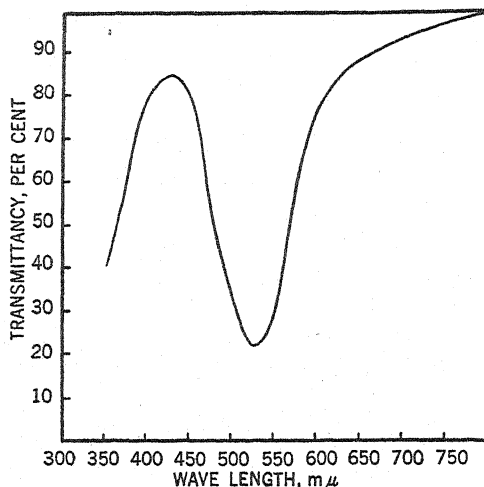


Fig. 4.—Transmission curve of potassium permanganate solution (approximately 0.002 per cent Mn).

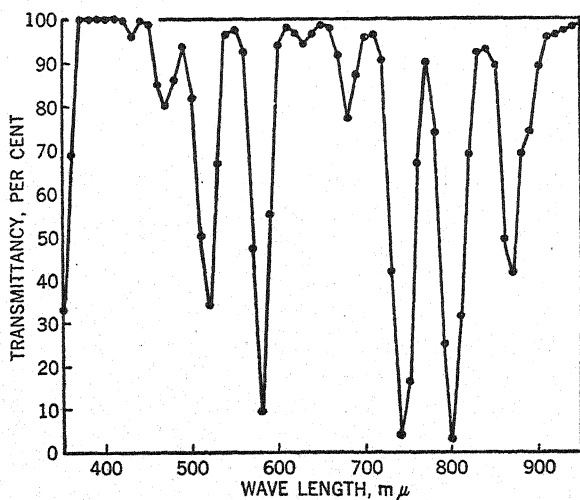


Fig. 5.—Transmission curve of neodymium nitrate solution (2.5 per cent neodymium). (According to C. J. Rodden, *J. Research Natl. Bur. Standards*, **26**, 557 (1941).)

$\log I_0/I$  is called the *extinction* (designated by  $E$ ) or the *density* of the solution. It is evident that a plot of extinction (at constant  $l$ ) against concentration gives a straight line if Beer's law is followed. This line



passes through the origin, since any absorption due to the solvent is cancelled out in the usual method of making the measurement (Fig. 6).

$E/l$  is usually known as the extinction coefficient.

### CLASSIFICATION OF METHODS

Two fundamentally different techniques are applied in determining the concentration of a colored substance in solution based on its absorption of light. The simplest method involves duplication of the color, i.e., matters are so arranged that the color of the sample solution is the same as that of a standard solution containing a known quantity of the constituent being determined.<sup>2</sup> This will be the case when the two solutions contain the same amount of colored substance in a column having the same cross section normal to the direction of examination (Lambert-Beer's law followed). The term *colorimetry* is usually applied to this technique, but it is a misnomer since no measurement of color is involved. Since the word, however, is commonly used by chemists to describe the process of color duplication or comparison it will be used in this sense here, and also as a general term to include any method for the determination of a substance by its color in solution. The second technique involves measurement of the absorption of light by a solution (liquid or gas) and may be called *absorptiometry*, but is generally known as *spectrophotometry* since light consisting of a restricted band of wave lengths is advantageously used.

<sup>2</sup> Usually it is the intensity of color that is duplicated, but sometimes it is the *hue* (see for instance the mixed-color dithizone methods).

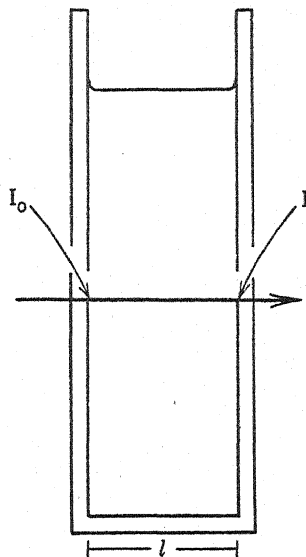


Fig. 6.—The solution of the colored substance is contained in a glass cell having plane parallel walls, and the light beam impinges perpendicularly on the face of the cell. Light is lost by reflection at the air-glass and glass-solution interfaces. If  $I_0$  is the intensity of the light beam entering the stratum of solution and  $I$  the intensity on leaving, the *transmittancy* of the solution is  $I/I_0$ . In practice the light transmitted by the cell containing the solution is compared against that transmitted by an identical cell containing water or a blank solution of the reagent. Alternatively the light transmitted by the cell filled with water is determined and subtracted from the light transmitted by the same cell containing solution.

Colorimetric and spectrophotometric methods may be sub-divided as follows:

I. Colorimetric

White light is ordinarily used for illumination and the condition of equal transmission of light by the standard and sample solutions is found in either of two ways:

A. Subjective

The observer relies upon his judgment of color intensities or hues; comparison tubes or cells, or a Duboscq colorimeter are used. See further p. 40.

B. Objective (Photoelectric colorimetry)

The photoelectric cell replaces the eye of the observer.

II. Spectrophotometric

Light consisting of a narrow band of wave lengths (ideally a "single wave length") is used, and the fraction of the incident light transmitted by the solution is measured by either of two methods:

A. Subjective

The intensity of the light which has passed through the solution is duplicated in a comparison beam by reducing the intensity of the latter in some suitable manner (use of a variable diaphragm, neutral wedge, etc.). The observer must match two halves of a field.

B. Objective (Photoelectric spectrophotometry)

A photoelectric cell (or cells) is used to measure the light transmission of the solution.

### SENSITIVITY

In colorimetric or spectrophotometric trace analysis, a knowledge of the sensitivity of the color reaction employed is of paramount importance, and it is necessary to have a simple method available for the expression of the sensitivity. The sensitivity of a color reaction may be defined as the smallest weight of substance that can be detected in a column of solution having a unit cross section. The weight may conveniently be expressed in micrograms and the area in square centimeters. This method of stating the sensitivity is based on the assumption that the law of Lambert-Beer holds to indefinitely low concentrations, so that the actual concentration of the colored product is immaterial. This assumption holds for the great majority of reactions in which the colored substance formed is soluble.

There are evidently two factors involved in the sensitivity thus defined, first, the intrinsic sensitivity which is proportional to the extinction coefficient of the solution of the colored product, and second, the ability of the

observer, directly or indirectly, to detect small differences in the light transmission of a solution. For comparative purposes the sensitivity could be defined in terms of the extinction coefficient of the solution for the wave length of maximum absorption.

The sensitivity of a color reaction according to the above definition will depend upon the method of color comparison or of transmission measurement. Two important cases, corresponding to IA and IIB of the classification above (p. 36), will be considered.

### Visual Colorimetry

The sensitivity is usually determined by using flat-bottomed tubes, one containing the blank solution, and the other variable amounts of the substance yielding the colored product together with the reagent. White light (daylight reflected from a white surface) is used for illumination. Such factors as the acidity, the excess of reagent and the time of standing must be specified. The quantity of substance ( $\gamma/\text{cm.}^2$ ) required to give a perceptible difference in appearance from the blank can be defined exactly only on the basis of probability. Thus the minimum amount might be defined as that which allows a detectable difference in appearance from the blank in 90 out of 100 comparisons. The determination of the limit thus defined would be laborious, and a less exactly defined and somewhat larger limit may be taken for all practical purposes, namely that which in practically every case will show a difference from the blank. A few such values are given in Table 4.

For low values of mass/ $\text{cm.}^2$ , the sensitivity determines the precision of the visual color duplication. The probability is great that the error of a single color duplication will not exceed  $(S/Q) \times 100$  per cent (where  $S$  is the sensitivity and  $Q$  is the weight of substance in micrograms per square centimeter cross-section of solution) as long as  $Q$  is less than 15 or 20  $S$ . When  $Q/S$  is greater than 15 or 20 the law of Weber applies and the precision remains constant over a wide range of  $Q$  values.<sup>3</sup> Cf. Fig. 7. In other words no useful purpose is served in working under conditions such that  $Q/S$  is larger than about 20. It has been stated that smaller absolute differences can be detected between two faintly colored solutions in an optimum concentration range than between a very faintly colored solution

<sup>3</sup> Weber's law states that the increase or decrease in stimulus required to produce a just noticeable difference in the resulting sensation bears a constant relation to the original stimulus, or expressed symbolically:

$$\Delta R/R = \text{constant, where } R = \text{magnitude of stimulus.}$$

In comparing color intensities in tubes according to the procedure described above, the value of  $\Delta R/R$  is usually found to be 0.05 — 0.07. See, for example, J. H. Yoe and F. H. Wirsing, *J. Am. Chem. Soc.*, **54**, 1866 (1932).

TABLE 4  
SENSITIVITIES OF COLOR REACTIONS<sup>a</sup>

Element	Reagent	Minimum Amount Detectable per $\text{Cm}^2$	
		Visually $\gamma$	Spectrophotometrically $\gamma$
Ag	<i>p</i> -Diethylaminobenzylidinerhodanine		0.01 (green filter)
	Dithizone		0.01 (yellow filter)
Al	Aurintricarboxylate ( <i>pH</i> 5.5)	0.01	0.002 (green filter)
	Alizarin S		0.003 (580 $m\mu$ )
As	Molybdate-hydrazine sulfate		0.01 (red filter)
Au	Stannous chloride (1 <i>N</i> HCl)		0.05
Be	Morin (fluorescence)	<i>ca.</i> 0.002	
	Quinalizarin	<i>ca.</i> 0.1	
Bi	Iodide		0.1 ( <i>ca.</i> 460 $m\mu$ )
Cb	Hydrogen peroxide (conc. $\text{H}_2\text{SO}_4$ soln.)	10	
	Quinalizarin (conc. $\text{H}_2\text{SO}_4$ soln.)	5	
Cd <sup>85</sup>	Dithizone ( $\text{CCl}_4$ )	0.03	
Ce	As $\text{Ce}^{++++}$	15	0.4 (blue filter)
Cl (free)	<i>p</i> -Aminodimethylaniline		0.004 (550 $m\mu$ )
Co	Nitroso-R salt	0.01	0.002 (green filter)
	Thiocyanate-acetone	5	
Cr	As $\text{CrO}_4^-$	1.0	0.01 (366 $m\mu$ ), 0.17 (436 $m\mu$ ), 0.4 (450 $m\mu$ )
	Diphenylcarbazine	0.03	0.002 (540 $m\mu$ )
Cu	Ammonia	10	0.8 (620 $m\mu$ )
	Dithizone ( $\text{CCl}_4$ )		0.005 (508 $m\mu$ ), 0.004 (red filter)
	Hydrochloric acid (9 <i>N</i> )	0.5	0.01 (436 $m\mu$ )
	Sodium diethyldithiocarbamate ( $\text{H}_2\text{O}$ )	0.05	0.01 (blue filter)
	Sodium diethyldithiocarbamate ( $\text{CCl}_4$ )		0.02 (blue filter); 0.01 (430 $m\mu$ )
Fe	<i>o</i> -Phenanthroline	0.05	0.005 (510 $m\mu$ )
	Thiocyanate ( <i>Cf.</i> p. 262).	0.1	0.01 (green filter)
Ga	8-Hydroxyquinoline (fluorescence in $\text{CHCl}_3$ )	0.1	
Hg	Dithizone ( $\text{CCl}_4$ )		0.008 (red filter)
In	8-Hydroxyquinoline ( $\text{CHCl}_3$ )		0.02 (400 $m\mu$ )
Ir		2	
Mg	Quinalizarin	0.1	0.017 (600 $m\mu$ )
	Titan yellow	0.05	0.006 (green filter)
Mn	As $\text{MnO}_4^-$	0.1	0.027 (522 $m\mu$ )
Mo	Thiocyanate-stannous chloride		0.03 ( $\text{H}_2\text{O}$ soln.) (blue filter), 0.015 (ether soln.) (blue filter)
$\text{N}(\text{NO}_2^-)$	Griess		0.0003 (520 $m\mu$ )

TABLE 4—(Continued)

Element	Reagent	Minimum Amount Detectable per $\text{Cm}^2$ .	
		Visually $\gamma$	Spectrophotometrically $\gamma$
N( $\text{NH}_3$ )	Nessler		0.003 (410 $\text{m}\mu$ )
Ni	Bromine-dimethylglyoxime	0.05-0.1	0.01 (green filter)
Os	Thiourea		0.1 (blue filter)
P	Molybdate-stannous chloride		0.001 (700 $\text{m}\mu$ )
Pb	Dithizone ( $\text{CCl}_4$ )		0.003 (520 $\text{m}\mu$ )
Pd	<i>p</i> -Diethylaminobenzylidinerhodanine (0.02 <i>N</i> HCl)	<0.05	
	Nitrosodiphenylamine	0.05	
Pt	Iodide		0.03 (blue-green filter)
	Stannous chloride		0.02 (blue filter)
Re	Thiocyanate-stannous chloride (ether solution)		0.005 (440 $\text{m}\mu$ )
Rh	Stannous chloride	0.5	<0.02 (blue filter)
Ru	Thiourea		0.05 (red filter)
	Phenylthiosemicarbazide	0.5	0.03 (blue filter)
Si	Molybdate		0.01 (390 $\text{m}\mu$ )
Te	Stannous chloride		0.05 (white light)
Ti	Hydrogen peroxide		0.07 (400 $\text{m}\mu$ ), 0.1 (450 $\text{m}\mu$ )
U	Hydrogen peroxide ( $\text{Na}_2\text{CO}_3$ soln.)		0.2 (520 $\text{m}\mu$ )
V	Hydrogen peroxide	2	0.17 (450 $\text{m}\mu$ )
	Phosphotungstic acid		0.027 (400 $\text{m}\mu$ ), 0.045 (440 $\text{m}\mu$ )
W	Thiocyanate-stannous chloride		0.2 (blue filter)
Zn	Dithizone ( $\text{CCl}_4$ )		0.004 (red filter), 0.0016 (green filter)
Zr	Alizarin		0.02 (560 $\text{m}\mu$ )

<sup>a</sup> For many reactions the sensitivity will depend on the conditions. Most of the sensitivities reported in this table pertain to the methods described in the text.

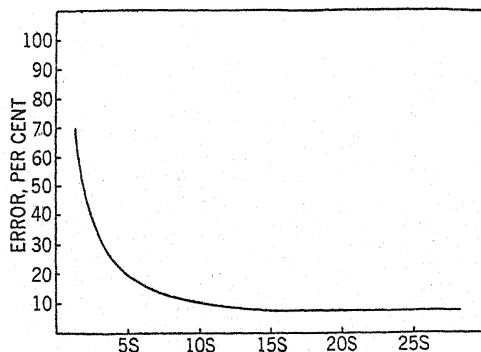


Fig. 7.—Maximum error in color comparison by the standard series method as a function of the amount of colored substance in a column of unit cross-section in terms of the sensitivity *S* of the reaction (p. 37). The error becomes constant at approximately 15 *S*.

and water. It is difficult to see why this should be true, and the experimental evidence on this point is not convincing.

### Photoelectric Spectrophotometry

The minimum amount of a colored substance that can be detected by photoelectric spectrophotometry usually does not depend upon the sensitivity of the light measuring apparatus, but instead upon the reproducibility of the measurement of the transmittancy of the faintly colored solution (this includes the precision of reading a scale or making a pointer setting). As a reasonable basis for the expression of the sensitivity it may be assumed that a difference of 0.001 in extinction can be detected with certainty. This value corresponds to a difference of 0.2 per cent in the transmittancies of the blank and sample solutions. Instruments in common use permit the attainment of a precision of 0.2 per cent in transmittancy determination without much difficulty.

Spectrophotometric sensitivities of a number of reactions, calculated from data in the literature, are given in Table 4.<sup>4</sup> The values represent the number of micrograms of element, converted to the colored product, which in a column of solution having a cross-section of 1 square centimeter shows an extinction of 0.001. The smallest amount of an element detectable in the most sensitive color reactions by photoelectric spectrophotometry usually lies in the range 0.001 to 0.01  $\gamma/\text{cm}^2$ . It may be noted that the upper limit of the molar extinction coefficients of the most strongly colored substances used in color methods seems to lie at about 35,000.<sup>5</sup>

Sensitivity values such as those given in Table 4 enable one to adjust the concentration or the length of column of solution to furnish the required precision in a determination, or to predict the precision under specified conditions.

### I. Colorimetry

Although the present practice in the quantitative use of color methods favors the application of spectrophotometry rather than colorimetry, the latter technique can still render good service in trace analysis, and indeed sometimes offers some advantages. The apparatus required in colorimetry is simple and inexpensive, the sensitivity and precision are frequently satisfactory and if only an occasional determination is to be run less time may be required than in a spectrophotometric method which will often necessitate the preliminary construction of a standard curve.

<sup>4</sup> If the molar extinction coefficient of the colored compound is known, the sensitivity as here defined is given by  $M/\epsilon$  where  $M$  is the molecular weight (in grams) of the compound. Expressed in terms of an element, the sensitivity is  $\frac{nM}{\epsilon}$  where  $n$  is the number of atoms of the element in a molecule of the compound.

<sup>5</sup> H. A. Liebhafsky and E. H. Winslow, *Ind. Eng. Chem., Anal. Ed.*, **11**, 189 (1939).

As already mentioned, the essential feature of colorimetric methods is the matching of the color of the sample solution with that of a comparison solution, so that when duplication is attained both solutions contain the same amount of the colored substance in columns of equal cross-section:

$$c_x l_x = c_s l_s,$$

where  $c_x$  = concentration of sample solution,

$l_x$  = depth of sample solution (in line of sight),

$c_s$  = concentration of standard solution,

$l_s$  = depth of standard solution.

Since  $c = \text{mass}/l^3$ , the dimensions of  $cl$  are  $\text{mass}/l^2$  or mass per unit cross-section.

If  $c_x l_x$  is fixed, there are evidently three ways in which this product can be duplicated if one starts with a standard solution of concentration  $c_s$  (Fig. 8):

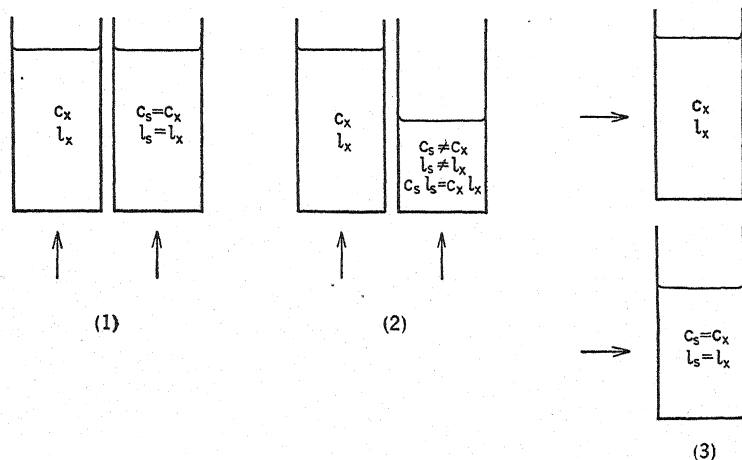


Fig. 8.—Schematic representation of methods used in arriving at the state of equilibration in colorimetry.

	Vary	Keep constant
Method (1)	$c_s, l_s$	—
Method (2)	$l_s$	$c_s$
Method (3)	$c_s$	$l_s$

Method (1) includes (a) the standard series method, and (b) the colorimetric titration or duplication method. In the standard series procedure a number of known solutions is prepared, each having the same volume as the sample solution and contained in identical tubes with flat bottoms. The sample and comparison solutions are treated with reagent at as nearly the same time as possible. This method of color comparison is the most sound in principle, because Beer's law need not hold, error from fading or slow

development of color is reduced to a minimum, and any effect of variable concentration of reagent is eliminated. The method is not as convenient as some others to carry out, however, for a comparatively large number of standards may have to be prepared. Sometimes the amount of constituent in the sample solution is roughly determined with a preliminary series (or by a colorimetric titration), and then more exactly by the use of a second series in which adjacent members differ by smaller increments.

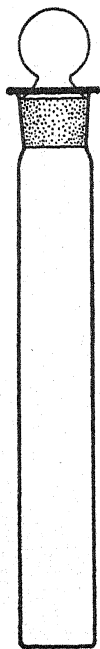


Fig. 9.—Tube for color comparisons.

Nessler tubes are generally less convenient to use in color comparisons in trace analysis than shorter and somewhat narrower tubes such as the one illustrated in Fig. 9. These tubes are provided with ground glass stoppers to permit their use in procedures involving extraction with immiscible solvents, and to facilitate mixing by inversion. It is convenient to have available two sizes of these tubes, namely  $1.8 \times 15$  cm. (25 ml.) and  $1.2 \times 8$  cm. (5 ml.).

Comparison of the solutions should be made in daylight by examining the tubes axially against a white background such as that obtained by inclining a white card at an angle of about 45 degrees in front of a window receiving light from the sky, but not directly from the sun. When layers of immiscible solvents are to be compared, the tubes are viewed at right angles to their axes against a white vertical background. The tubes should be interchanged during the examination when the colors are very similar, because to some observers the tube on one particular side will always appear a little more strongly colored than that on the other when the color intensities are actually the same.

An observer can usually differentiate without hesitation between two solutions when the amounts of colored substance in columns of equal cross-section differ by about  $\frac{1}{15}$  (or 7 per cent) in the optimum range where Weber's law applies. As a rule no useful purpose is served in having adjacent members of the standard series differ by less than 10 or 15 per cent. As a matter of fact, standards differing by 20 per cent will serve satisfactorily. With such a series an experienced observer can usually find the content of the sample within 5 per cent. Suppose  $X$  (the sample) contains 11.2  $\gamma$  of constituent, and the two adjacent standards contain 10 and 12  $\gamma$ . The observer will probably have difficulty in deciding whether  $X$  is closer to one or the other of the standards, or at least will see that it is very close to being midway between the two, and he will call the content 11  $\gamma$ . If  $X$



contains 11.6  $\gamma$  he probably will be unable to distinguish  $X$  from the 12  $\gamma$  standard and will call the amount of constituent present 12  $\gamma$ , and the error will still be less than 5 per cent. If the amount of constituent is very small, then the standard solutions may contain respectively 0, 2S, 4S, 6S, 8S and 10S micrograms of the constituent per square centimeter of cross-section ( $S$  is the sensitivity as defined on p. 37).

In the colorimetric titration method a standard solution of the constituent being determined is added to a tube or other suitable vessel containing water and reagent until the color is the same as that of a second tube containing the sample solution which has been treated with reagent. The tubes are examined axially. The standard solution of suitable strength is conveniently added from a microburet subdivided to 0.01 ml. The volume of the two solutions should be approximately the same at the end. A difference of 10 per cent or so is usually of no importance. The tubes should be checked for equal diameter. The tubes mentioned above may be used to advantage in colorimetric titrations if the volume of solution is not too great. Mixing may be accomplished simply by shaking the tubes or, if necessary, by the use of a glass rod. It is hardly necessary to slip a cylinder of black paper around the tubes to exclude extraneous light as sometimes recommended.

In order that this method may yield accurate results it is necessary that the manner of mixing the reagent and the solution of the reacting constituent have no effect upon the color. Moreover the color development must be very rapid,<sup>6</sup> and the colored product must be stable. Thus the colorimetric titration method is not to be recommended for the determination of iron by the thiocyanate method, because the color of the thiocyanate complex fades fairly rapidly on standing. Even if the conditions mentioned are not entirely fulfilled, the colorimetric titration technique may at times be used to advantage in connection with the standard series method. The approximate amount of the constituent in the sample solution can first be found by colorimetric titration, and then a series of standards covering a narrow range can be used to fix the amount more precisely, a new aliquot of the sample solution being used if necessary. The titration technique is generally to be preferred to the standard series method whenever it is applicable and only one or two analyses are to be made.

The following procedure is advantageously followed in finding the amount of constituent required for equicoloration in colorimetric titration. The standard solution is added to tube  $S$  (standard) until it is seen that the

<sup>6</sup> This requirement can often be circumvented by using a standard solution containing the constituent in the form of the colored product. Thus in determining manganese as permanganate, a solution of potassium permanganate can be used as the standard.

color intensities are nearly the same. The standard is now added in small increments with comparison after each addition, and the amount noted which corresponds to the last definite difference between  $X$  and  $S$ . The addition of standard is continued until  $S$  is definitely stronger in color than  $X$ . If  $a_1$  is the amount of standard for which  $S$  is just weaker than  $X$ , and  $a_2$  is the amount for which  $S$  is just stronger than  $X$ , the amount of constituent in the sample solution is taken to be  $\frac{a_1 + a_2}{2}$ . The error should not exceed 5 per cent.

Method (2), usually called the balancing method, is the one used with the Duboscq colorimeter. The chief advantage of the method lies in the ease with which  $l_s$  (or  $l_x$ ) can be varied and exactly measured to arrive at the state of equicoloration. Beer's law is assumed to be obeyed.

The Duboscq colorimeter is of restricted value when a very low concentration of substance is to be determined, because the value that can be given the product  $c_x l_x$  is limited by the height of the cups (about 5 cm.). Frequently in trace analysis the sample solution will have a comparatively large volume, and in such a case color comparison tubes must be used instead. It may also be noted that the Duboscq colorimeter can not be employed when the reagent or solvent is appreciably colored. The absorption of light by water in layers a few centimeters thick is too small to have any effect.

In using a colorimeter the following precautions should be taken. It should be ascertained whether each scale reads zero when the plunger touches the bottom of the cup. Cups must not be changed from one side to the other. Cups and plungers must be scrupulously clean. The optical perfection of the instrument should be tested by filling both cups with a standard solution of the colored substance being determined, setting one cup at a height which gives a suitable color intensity and permits the depth to be read with small percentage error, then moving the other cup until the two halves of the field appear the same, and repeating the balancing until a total of about 10 readings has been obtained. The average reading should agree with the setting of the stationary cup within 1 or 2 per cent. If this is not the case the reading of the unknown solution can be corrected with the aid of the ratio that has been determined. Alternatively, if the optical perfection of the instrument is in doubt one can proceed in the following manner. One of the cups, say  $L$  (the left), is filled with standard solution and set at a convenient height. Cup  $R$  is filled with the same standard solution and the average of 10 settings of  $R$  found; cup  $R$  is emptied, rinsed with the unknown (sample) solution and then filled with the latter. The point of balance is found by moving  $R$  and averaging a sufficient number of readings. The concentration of the unknown solution then is  $c_x = R_s/R_x$ .

$\times c_s$ ,  $R_s$  and  $R_x$  being the average readings given by the standard and unknown solutions in the right hand cup, the other cup being kept stationary.

Either daylight or artificial light of proper color quality may be used for illumination. The white glass plate beneath the cups should be set at the angle giving the optimum illumination when daylight is used; this plate must be kept clean or else the two halves of the field may appear of different color intensities when a balance should exist, or it may be impossible to match two solutions because of a difference in hue. The same difficulties may be encountered if any other surfaces in the optical paths become dirty or dusty.

Methods have been described in which the standard solution is replaced by a solid having a color simulating that of the solution of the colored substance. For example, a colored glass plate or a film of gelatin on glass

TABLE 5  
PRECISION OF COLOR INTENSITY DUPLICATION WITH THE DUBOSQ COLORIMETER

Solution	$\frac{Q}{\gamma/\text{cm}^2}$	Average Deviation of a Single Setting %
$\text{K}_2\text{CrO}_4$	10 Cr	6
	20	2.5
	60	1.1
	100	0.8
	300	1.8
$\text{Fe}^{+++} + \text{CNS}^-$	10 Fe	0.8
$\text{NiCl}_2$	35000 Ni	0.6
$\text{Cu}^{++} + \text{NH}_4\text{OH}$	100 Cu	1.0

can be used for the purpose. In another method the use of a standard solution is dispensed with by using monochromatic light of suitable wave length and varying the depth of the colored solution until the color matches that of a smoked glass or fine wire gauze having an optical density of 0.5.<sup>7</sup>

The precision of color comparison with a Dubosq colorimeter may be described by giving the average deviation of a single setting of a cup. Table 5 contains some data on the precision of comparison for solutions of different colors and, in the case of potassium chromate, for different concentrations. The second column of the table shows the quantity of the element in a column of solution having a cross-section of 1 square centimeter. The average deviations given in the third column of the table were obtained in each instance from a series of 10 settings. Daylight (cloudy western sky in the afternoon) was used for illumination. So far as these results permit generalization, it may be concluded that the hue of the solution plays a

<sup>7</sup> A. Dognon, *Compt. rend. soc. biol.*, **129**, 467 (1938).

minor role in the precision of matching. At suitable color intensities the average deviation is substantially the same for red, yellow, green and blue colors, and is slightly less than 1 per cent on the average. It should be pointed out that the brightness of the field is an important factor in the precision of matching. At low light intensities the average deviation becomes greater. For this reason the use of filters with a Duboscq colorimeter in the comparison of faintly colored solutions is of dubious value.

At sufficiently low color intensities (below the range in which Weber's law applies) the average deviation corresponds to a constant amount of the colored substance which is related to, but obviously smaller than, the sensitivity  $S$  that has already been referred to (p. 37).<sup>8</sup> For potassium chromate this constant amount is approximately  $0.5 \gamma$  Cr per  $\text{cm}^2$ . This quantity is important since it is an index of the precision with which small amounts of a constituent can be determined with a Duboscq colorimeter. In obtaining the net precision of the comparison of an unknown solution against a standard solution it must be remembered that it is actually necessary to make two comparisons, namely the standard against a fixed solution (standard) and the unknown against the same solution to avoid error due to differences in the two halves of the instrument. Suppose one desires to know what precision may be expected in determining  $20 \gamma$  of Cr as chromate in 10 ml. of solution by the use of the Duboscq colorimeter. Assume for simplicity that the solution fills the colorimeter cup to a height of about 5 cm., the maximum possible. Then  $Q = 10 \gamma/\text{cm}^2$  and the average deviation of a setting is 6 per cent according to Table 5. If ten settings are made of standard against standard, and of unknown against standard, the net average deviation (error) of the ratio standard/unknown will be  $\frac{\sqrt{2} \times 6}{\sqrt{10}}$

or 2.7 per cent. By referring to a probability table, it may be found that the probability of the average lying within 5 per cent of the truth is 0.7, a figure which does not carry much conviction. But the probability that the average is in error by less than 10 per cent is 0.96. This figure is sufficiently favorable to allow a reasonable expectation that the precision of the comparison will correspond to an error of 10 per cent or less. Whether the same *accuracy* can be obtained will depend upon such factors as the stability of the colored compound, the reproducibility of the color system and its

<sup>8</sup> It may have occurred to the reader that the quantity  $S$  (p. 37) may be obtained from the average deviation in the comparison of two very faintly colored solutions of the substance in question. If  $q$  is the amount of material in a column of solution of unit cross-section corresponding to the average deviation, it is readily shown that a deviation as large as twice the average deviation will be encountered only once in 10 observations on the average, or in other words in 9 times out of 10 the stronger solution will appear more strongly colored to the observer and  $2q$  might be taken as defining  $S$ . The  $S$  so obtained might not be quite the same as the  $S$  for color comparison tubes because of the different conditions of comparison.

adherence to Beer's law, to say nothing of the effect of foreign substances. Moreover, the accuracy may depend upon the relative thicknesses of the standard and sample solutions at the balance point.

Method (3), sometimes called the dilution method, has found little use in colorimetry, but can be applied to advantage at times (*cf.* p. 52) in the colorimetry of traces. Application may be made of it in extraction methods if the reagent is colorless (or is not extractable if colored). For example, the aqueous solution can be shaken with a small volume of the immiscible solvent in a glass-stoppered tube, and more of the solvent then added from a buret until the layer of the organic solvent shows the same color intensity as that in the unknown tube when the tubes are examined at right angles to their axes.

Since the concentration of the reagent is not the same in the sample and standard solutions at the point of balance, the concentration of the constituent may not be the same in the two solutions in spite of the equal color intensities if the excess of reagent has an effect upon the color intensity. This method must therefore be used with caution.

### Photoelectric Colorimetry

The photoelectric cell may be used instead of the eye to determine the point of equi-coloration. Two of the methods mentioned on p. 41 have been applied in photoelectric colorimetry, namely (2) and (3). A photoelectric colorimeter on the principle of the Duboscq visual instrument has been described.<sup>9</sup> If optical difficulties in the construction of such an instrument are surmounted, it should have definite usefulness. Such an instrument is in theory superior to a photoelectric filter photometer working at constant depth of solution in one respect, namely that heterochromatic light will not cause apparent deviations from Beer's law. Practically this is true if the two photocells have equal spectral sensitivities. Since filters are commonly used to supply a restricted band of wave lengths this condition should not impose any serious obstacle.

A double photocell filter photometer may be used as a photoelectric colorimeter as described on p. 54 and such a procedure sometimes possesses definite advantages in trace analysis.

## II. Spectrophotometry

Spectrophotometric methods have a number of advantages over the colorimetric. The sensitivity may be increased by measuring the absorption of a solution at the wave length of minimum transmission. If a photoelectric cell is used, measurements may be made in the ultraviolet or infrared. It is possible to avoid or minimize the effect of foreign colored

<sup>9</sup> A. Goudsmit, Jr. and W. H. Summerson, *J. Biol. Chem.*, **111**, 421 (1935); G. Bernheim and G. Revillon, *Ann. fals.*, **29**, 5 (1936).

substances by working at suitable wave lengths. Higher precision can be obtained in photoelectric spectrophotometry than in ordinary colorimetry. Moreover, when many determinations are to be made, objective spectrophotometric methods are more rapid and less fatiguing than the subjective colorimetric.

A detailed account of the instruments used in spectrophotometry is beyond the scope of this book, and the discussion here will be limited to brief, general considerations, with special reference to the methods of measurement.

As the name indicates, a spectrophotometer is an instrument for measuring the intensity of the light of various wave lengths transmitted (or reflected) by a solution (or other medium). It consists essentially of a device (monochromator or diffraction grating) for furnishing "monochromatic light", one or more absorption cells for holding the sample and reference solutions, and a photometric arrangement for the subjective or objective measurement of the intensity of the transmitted light. Instead of a monochromator, color filters may be used to furnish more or less narrow bands of wave lengths from a continuous light source. Such an instrument is called a *filter photometer*, or sometimes an *abridged spectrophotometer*.

### Visual Instruments<sup>10</sup> and Methods

Briefly, these instruments (frequently filter photometers) function in the following manner. Two beams from the same light source, one passing through the solution whose transmittancy is being measured, the other usually passing through a comparison cell containing water or a solution of the colored component, are brought together in such a manner that the observer sees two halves of a field illuminated by each. The amount of light in the comparison beam is reduced by one of the following methods so that it becomes equal to that in the other beam, and the two halves of the field of view show the same color intensity:

1. The aperture is varied by means of a diaphragm or slit.<sup>11</sup>
2. The light passes through two polarizing prisms, one of which can be rotated to vary the amount of light transmitted.
3. A neutral light-absorbing wedge, movable in the direction of its length, is used (in combination with a compensating wedge to furnish uniform density).

<sup>10</sup> For a brief account see R. H. Müller, *Ind. Eng. Chem., Anal. Ed.*, **13**, 706 (1941); T. R. P. Gibb, Jr., *Optical Methods of Chemical Analysis*. McGraw-Hill, New York, 1942; pp. 79 and 141.

<sup>11</sup> C. Pulfrich, *Z. Instrumentenk.*, **45**, 35, 61, 109, 521 (1925). For applications see: C. Urbach, *Stufenphotometrische Absorptionsbestimmungen in der medizinischen Chemie*. E. T. Haim, Vienna, 1932; L. Heilmeyer, *Medizinische Spectrophotometrie*. G. Fischer, Jena, 1933; S. E. Q. Ashley, *Ind. Eng. Chem., Anal. Ed.*, **11**, 72 (1939).

These instruments may be graduated to read transmission, absorption, or extinction. An advantage of these instruments over some photoelectric filter photometers employing barrier-layer cells is the possibility of using highly selective filters, which would not transmit sufficient light for use with the latter.

It is usually necessary to prepare a standard curve in using an instrument of this type for determining the concentration of the unknown. If the solution of the colored component follows Beer's law and if the light transmitted by the filter is sufficiently "monochromatic," a plot of extinction against concentration gives a straight line (see p. 34). The precision attainable in the favorable range of extinction is governed by Weber's law. Under the most favorable conditions, a difference of approximately 1 per cent in the brightness of the two juxtaposed fields can be detected by a trained observer. The error in concentration determination as a function of the extinction is given by:

$$\frac{dc}{c} = -\frac{0.43}{E} \frac{dI}{I}$$

If Weber's law held for very low light intensities and there were no instrumental limitations, the accuracy would be greater the larger the extinction. Actually, visual spectrophotometers give the most precise results when the transmittancy is 10 to 20 per cent, and from the preceding expression it is seen that an error of 1 per cent in determining the transmittancy in this range causes a corresponding error of about 0.5 per cent in the calculated concentration. When the transmittancy is 90 per cent the error in concentration should be about 10 per cent on the same basis. Naturally the precision can be increased by making a number of readings and taking the average, as is done in the use of the Duboscq colorimeter. The precision attained in practice is graphically represented in Fig. 10.

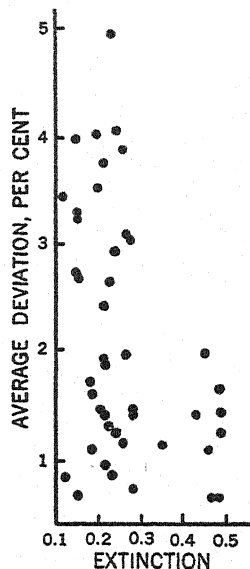


Fig. 10.—Error in visual photometry of various solutions as a function of extinction (partial reproduction of a figure given by Ashley, *Ind. Eng. Chem., Anal. Ed.*, 11, 75 (1939)).

### Photoelectric Spectrophotometric Methods

In recent years the use of photoelectric cells in photometry has attained great popularity. There are numerous photoelectric photometers for

colorimetric analysis on the market. Many of these are filter photometers. Some instruments employ barrier layer photocells, others the emission type. A detailed description of the various instruments with discussions of their use may be found in the literature.<sup>12</sup>

Photoelectric methods applied in colorimetric analysis may be classified as follows:

1. Single photocell methods

- a. Ordinary

- (1) A cell containing water or diluted reagent solution is placed in the path of the light beam, which impinges on a photoelectric cell. The photocurrent produced is measured by some suitable arrangement (a low-resistance microammeter may, for example, be used with a photronic cell), and its magnitude is a measure of the light intensity  $I_0$ . An identical cell containing the solution of the colored component is now substituted for the blank cell and the intensity,  $I$ , of the beam measured. If the response of the photocell is linear, the respective photocurrents give the transmittancy  $I/I_0$ . The chief requirement to be fulfilled in this method is constancy of the light source during the interval the two photocurrents are measured. Linear response of the photocell is desirable, but not essential if a standard curve is used in finding the concentration of the sample solution, as is generally the case.

- b. Flicker

By a suitable device a light beam is sent rapidly alternately through the reference and sample solutions, and the resultant beams are balanced, as indicated by the absence of a pulsating photocurrent.

2. Double photocell methods

In these methods the difference in intensity of two light beams is measured. Fluctuations in the light source are automatically compensated if a circuit of proper design is employed.

- a. Two light beams from the same source are passed respectively through the reference and sample solutions and allowed to strike the respective photocells. The net response of the cells is a measure of the light absorbed by the sample solution, if the cells were adjusted for equal response initially. The current of the opposed

<sup>12</sup> For a comprehensive account of photoelectric methods in analytical chemistry, with many references, see R. H. Müller, *Ind. Eng. Chem., Anal. Ed.*, **11**, 1 (1939); also see G. Kortüm, *Angew. Chem.*, **50**, 193 (1937). A discussion will also be found in T. R. P. Gibb, Jr., *Optical Methods of Chemical Analysis*. McGraw-Hill, New York, 1942.



cells may be measured directly by deflection, or one photocell may be balanced against the other by a suitable circuit arrangement, the galvanometer then being used as a null instrument. Both photocells must show linear response, and should have identical color sensitivity if the light is not monochromatic.

- b. The arrangement is the same as in (a) except the amount or intensity of light in the reference beam is reduced by means of a variable diaphragm or other device until the net response of the photocells is zero.

Some observations may be made on some of these methods. One well-known instrument frequently used, especially in clinical work, utilizes the system mentioned in 1 a (1) above. It is a filter photometer with a barrier-layer cell, and a microammeter for reading the photocurrent. A constant-current transformer feeds the tungsten lamp. The absorption cells are placed in a sliding carriage movable at right angles to the path of the beam of light from the lamp to the photocell. Briefly, the following procedure is used in determining the transmittancy of a solution. A suitable filter is put into place in front of the photocell, and two parallel-walled absorption cells are respectively filled with the solution of the colored component and the blank or reference solution (either water or reagent solution having the same concentration as in the unknown). These cells are placed next to each other in the carriage, with the reference cell in front of the photocell. The light is switched on and the microammeter put into the circuit. The iris diaphragm between the light source and the reference cell is adjusted so that the microammeter reads approximately 100. The reading will be found to decrease quite rapidly at first, but after a few minutes the ammeter needle becomes virtually stationary, and the iris diaphragm is then carefully adjusted so that the meter reads 100.0 (corresponding to 100 per cent transmission). The carriage is now quickly moved to bring the colored solution in front of the photocell, and the microammeter read immediately (to 0.1 division by estimation). The value obtained is the percentage transmittancy. The reading is repeated as many times as the required precision calls for, the reference solution transmission being adjusted to 100 each time. If the line voltage does not show too great fluctuations, readings can be reproduced in most cases to 0.2 scale division. Under constant illumination the current given by the photocell slowly decreases as a result of "fatigue," but the change is so slow that no appreciable error results if the reference and sample solutions are read within a few seconds of each other.

With one of the common types of double cell photometer there are a number of ways in which a measurement can be made:

1. **Deflection Method.**—Both absorption cells are filled with water, and

one or both iris diaphragms are adjusted until the galvanometer shows no deflection. One of the photocells (say the right) is shaded and the resistances adjusted so that the ammeter reads 100 (meaning 100 per cent absorption). The solution whose absorption is to be measured is placed in the right hand cell and illuminated. The reading obtained is the percentage absorption.

**2. Compensation Method.**—The absorption cells are filled with water, and one of the iris diaphragms (left) is opened so that it reads zero. The opening of the other iris diaphragm is varied until the galvanometer gives no deflection. The solution being measured is substituted for the water on the right side, and the galvanometer restored to null by varying the opening of the right hand diaphragm. The reading of the latter gives the absorption.

**3. Duplication Method.**—This method is really a colorimetric one, but it is included here for the sake of convenience. One may proceed in one of two ways:

*a. Duplication by Substitution.*—The null point of the instrument is obtained as in the deflection method, the sample solution is placed in the right cell and the resistance is altered to give a reading of 100 or other large value. A cell containing a measured volume of reagent solution is substituted for the sample solution and a standard solution of the constituent is added from a buret until the deflection is the same as with the sample solution. If  $V$  is the volume of the reagent solution,  $v$  the volume of standard solution required for duplication and  $c$  its concentration, the concentration of the sample solution is  $\frac{cv}{V + v}$ .

*b. Duplication by Direct Comparison.*—The zero point of the instrument is obtained at full sensitivity, one absorption cell is filled with the sample solution treated with reagent and the cell on the other side is filled with a known volume of diluted reagent solution. A standard solution of the constituent being determined is added to the latter until the galvanometer again reads zero. If the spectral sensitivity of the two photocells is not the same, the initial zero point adjustment must be made with the colored solution of the sample in both absorption cells.

Before considering the relative merits of the various methods involving the use of photocells, a few words may be said in general about the relation between the error in the measurement of transmittancy or absorption and the resulting error in concentration. The error in concentration arising from a given error in the determination of the transmittancy of the solution may be calculated from the expression given on page 49, which shows that the former error is a function of the extinction of the solution. If the

error in the transmittancy is 1 per cent absolute, the corresponding error in concentration is as follows:<sup>13</sup>

$I$ Per cent	$dc/c$ Per cent
90	10.7
80	5.6
70	4.0
60	3.3
50	2.9
40	2.7
30	2.8
20	3.2

The most favorable transmittancy range is 20 to 60 per cent, over which the error remains nearly constant. In trace analysis the analyst is frequently forced to work with solutions having transmittancies greater than 80 per cent. The concentration error (in per cent) in the range 80 to 100 per cent is for all practical purposes given by  $\frac{100}{100 - I} dI$ .

The deflection method with double photocells requires a constant light source, just as does the ordinary single cell method. With a properly designed balancing circuit this requirement is eliminated, or at least reduced to the extent that small variations in source intensity are without appreciable effect. Under favorable conditions the error in reading the scale becomes the major one. The error in setting the microammeter needle at 100 and making the transmittancy or absorption reading should not exceed 0.2 scale division, which represents an error of 0.6 per cent in concentration at 50 per cent transmittancy, if it is assumed that the standard curve is not in error. At 95 per cent transmittancy the corresponding concentration error will be 4 per cent.

In the compensation method, slight fluctuations in the source have little effect and the limiting factor is likely to be the accuracy of the compensating device and the precision with which it can be read, provided proper attention is paid to overshooting and fatigue phenomena of the barrier-layer photocells. A sufficient length of time must be allowed to elapse before final adjustment of the compensating device, and unnecessary alteration in the illumination of the compensating photocell is to be avoided. In general practice this method has no advantage over the deflection method if a constant light source is available.

<sup>13</sup> These values hold only when the relation between concentration and extinction is linear. If Beer's law is not followed, the error in concentration corresponding to a given error in transmittancy must be found with the aid of a curve in which absorption is plotted against  $\log c$ . See A. Ringbom, *Z. anal. Chem.*, **115**, 332 (1938/39).

Duplication methods have certain advantages. Real or apparent deviations of the color system from Beer's law do not matter. When only a few determinations are to be made, the duplication technique has the advantage that a standard curve need not be constructed. In duplication by substitution (3a) slight variations in source intensity may have a marked effect. In contrast to all the other methods, the method of direct comparison between sample and standard (3b) permits use of the full sensitivity of the photocells, which is a fact of importance in trace analysis. Moreover, in this method small variations in the intensity of the source have hardly any effect. Ringbom has recommended this procedure and given results of its use.<sup>13</sup> When using a yellow filter and a clear 5-watt lamp, Ringbom found that his instrument (a barrier-layer cell photometer) at full sensitivity gave a deflection of 9 scale divisions for a 1 per cent change in absorption. In other words if the scale error in the color duplication is 0.5 division (the error in careful work), the error in the transmittancy will be about 0.05 per cent, and this corresponds to an error of approximately 0.15 per cent in the concentration when the transmittancy is 50 per cent. If the transmittancy of the solution is 0.95, the concentration should be determinable to 1 per cent or thereabouts, provided the reproducibility remains approximately the same at low extinction values. Naturally this deduction rests on good reproducibility and stability of the colored product (cf. p. 60), but the result indicates what may be expected under favorable conditions. For other than yellow filters the sensitivity becomes smaller, since the barrier-layer cell shows decreased sensitivity at other wave lengths. Ringbom gives the following figures for some other filters (values are deflections in scale divisions for 1 per cent absorption):

Green	5.0
Blue-green	4.6
Red	4.0
Blue	1.1
No filter	9.4

It may be pointed out that it is not possible to increase the differential sensitivity of two phot cells by using a more intense light source or a more sensitive meter, because there is a limit to the constancy of the current yielded by them. The current becomes more variable at high light intensities and the zero point shifts. The results are more reproducible when light filters are used to cut down the intensity of the illumination, and when the solution absorbs fairly strong. From the standpoint of trace analysis a study of the limits of the measurements of slight differences in transmittancy by this method is desirable.

## Filters

Except when there are good reasons to the contrary the transmittancy of a dilute solution should be determined at the wave length of minimum transmittancy, in order to obtain maximum sensitivity. When a spectrophotometer is used, the wave length, or rather a narrow band of wave lengths, can be selected at will with the aid of a monochromator. This is the ideal arrangement but it is possible to obtain good results by the use of a filter photometer. It is a fortunate fact that solutions of most of the determination forms used in colorimetric analysis show broad absorption bands, and with such solutions suitable filters will in many cases yield practically the same results as a monochromator. The filters used with a filter photometer are commonly glass,<sup>14</sup> but gelatine filters (stained gelatine films mounted between glass<sup>15</sup>) are also useful. Suitable solutions placed in cells find occasional application.<sup>16</sup> Gelatine filters are sensitive to heat, and the transmission characteristics of some may be markedly changed on continued exposure to strong light. With some exceptions glass filters are stable to the action of light. As already mentioned, highly selective filters can not be used with some types of photoelectric photometers because of the small amount of light transmitted by such filters.

Apparent deviation from Beer's law may occur if the light used in absorptiometry is not monochromatic. If the principal wave lengths of the illuminating light are restricted to one side of an absorption band as illustrated in Fig. 11, a linear relation between extinction and concentration will not be obtained, even if Beer's law actually holds. Yellow solutions sometimes do not appear to obey Beer's law because the blue or violet filters used may not be sufficiently selective. Even when a monochromator is employed, deviations from linearity may occur if the absorption maxima are very sharp and the slit width is too great or there is stray or scattered light in the emergent beam. On the other hand, it is easy to obtain a close approximation to linearity between extinction and concentration if the absorption band is broad and it does not occur at the ends of the visible spectrum, because suitable filters can then be obtained without much difficulty. Thus in the case of potassium permanganate solutions, which

<sup>14</sup> See Corning Glass Works, *Glass Color Filters*; Fish-Schurman Corporation, *Jena Colored Optical Filter Glasses*; Hodgman and Lange, *Handbook of Chemistry and Physics*; *International Critical Tables*, Vol. 5, p. 271 (1929). For a series of filters suitable for use with a neutral wedge photometer see P. A. Clifford and B. A. Brice, *Ind. Eng. Chem., Anal. Ed.*, **12**, 218 (1940).

<sup>15</sup> Eastman Kodak Company, *Wratten Light Filters*.

<sup>16</sup> Formulas for the preparation of selectively absorbing solutions may be found in *International Critical Tables*, Vol. 7, p. 160 (1929), and in a paper by E. J. Bowen, *J. Chem. Soc.*, **1935**, p. 76.

have a broad absorption band in the green, a green filter whose transmission curve is more or less inversely symmetrical to those of the permanganate solutions will give a straight line relation or a very close approximation thereto. If the transmission curve of a colored solution is available, the proper wave length of illuminating light or filter may be chosen with exactness. If transmission data are not available, it sometimes suffices to choose a filter whose color is as close as possible to the complementary color of the solution. Occasionally one will go astray in using this method

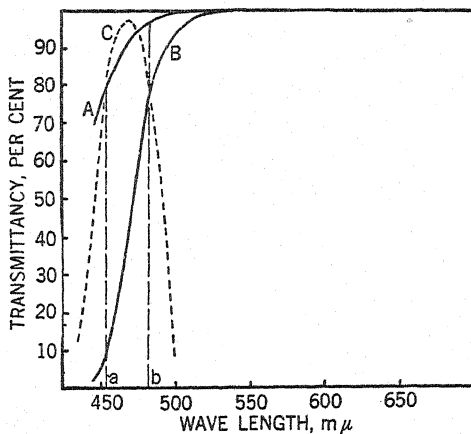


Fig. 11.—Illustrating the apparent failure of Beer's law when a blue filter is used in determining the transmittancy of potassium chromate solutions. *A* is the transmission curve of *ca.* 0.5 p.p.m. Cr solution, *B* the curve of *ca.* 5 p.p.m. Cr solution and *C* the transmission curve of the filter. Suppose the light transmitted by the filter to consist of two wave lengths *a* and *b*. Evidently the sum of transmitted *a* and *b* will be greater for *B* than it should be in comparison with *A* because the difference in transmittancy between the two solutions is greater for *a* than for *b*. The situation is the same for any other two similar wave lengths transmitted by the filter. Consequently the extinction is less than it should be at the higher concentrations, and a plot of extinction against concentration will give a curve concave downwards. The extent of deviation from a straight line will depend on the sensitivity of the photocell for light of various wave lengths.

(neodymium nitrate, Fig. 5). If several filters are available, the one giving the lowest transmittancy with a given solution is usually the one to use.

If the solution is colored by a foreign substance or if that substance develops a color when the reagent is added, it may be possible to find a wave length at which the compound of the constituent being determined absorbs strongly (not necessarily at the peak of the absorption curve) but at which the foreign substance absorbs only slightly; the transmittancy of the solution would then be measured at this wave length and the foreign substance would interfere only slightly. If a solution contains two colored substances

having considerably different absorption curves it may be possible to determine both substances by measuring the transmittancy of the solution at two suitable wave lengths and calculating the concentrations from the known extinction coefficients. An example is given on p. 121. Obviously a monochromator is superior to filters in these cases. If the latter are used calibration curves are constructed.

### Standard Curves

The common method of using the filter photometer or the spectrophotometer involves the construction of a standard curve (reference or calibration curve) for the constituent being determined. For this purpose suitable quantities of the constituent are taken and treated in exactly the same way as the sample solution for the development of the color and the measurement of the transmittancy at the optimum wave length.<sup>17</sup> The extinction ( $\log I_0/I$ ) is plotted against the concentration of the constituent.<sup>18</sup> A straight line is obtained if Beer's law is followed and if there are no complications due to the heterochromaticity of the light. This curve may then be used in future determinations of the constituent under the same conditions. When extinction is directly proportional to concentration only a few points are needed to establish the line. A greater number of points will generally be required when the relation is not linear.

It is advisable to check the standard curve at intervals. This may be done sufficiently well in most cases by verifying the position of one of the points situated some distance from the origin. When a filter photometer is used, the characteristics of the filter and the light source may change with time and the standard curve may be altered. Moreover in certain procedures the color intensity will depend upon the concentration of the reagent and if the latter undergoes a change with time the standard curve may have to be checked at the time the determination itself is run.

Only the most sanguine user of a spectrophotometer will calculate the concentration of his colored solution from the observed extinction and the value of the extinction coefficient taken from the literature. Such a pro-

<sup>17</sup> It may be mentioned that as a matter of convenience the transmittancies of the sample and standard solutions are usually obtained with respect to water in the reference cell. In plotting the standard curve it is customary to assign a transmittancy of 100 per cent to the blank solution (reagent solution plus water), which represents zero concentration of the constituent, in order that the curve may pass through the origin. In some instances it is advantageous to use the blank solution in the reference cell. This would, for example, be preferable in measuring the transmittancy of an acid solution containing iodide. The error due to slow liberation of iodine by air-oxidation would thus be cancelled out.

<sup>18</sup> Semi-log paper may be used if preferred for the plotting in order to avoid converting transmittancies into extinctions.

cedure demands the use of light of great spectral purity. It is very difficult to determine the absolute value of an extinction coefficient to within  $\pm 1$  per cent, whereas determination of the concentration of a solution by comparison against a similar standard can be made to within a few parts per ten thousand under the same conditions.<sup>19</sup>

As an example of the accuracy attainable with a photoelectric spectrophotometer when used with a standard curve, the results obtained by von Halban and Zimpelmann<sup>20</sup> in the determination of ferric iron with thiocyanate may be given. In spite of the shortcomings of this colorimetric reaction (fading of the color and non-conformance to Beer's law), iron in concentrations of 1:50,000 to 1:50,000,000 could be determined with an error of less than 1 per cent in all cases except one:

Iron present mg.	Iron found mg.	Error %
0.938	0.938	0
0.762	0.760	-0.26
0.3050	0.3047	-0.1
0.1335	0.1338	+0.25
0.0405	0.0407	+0.5
0.01010	0.01002	-0.8
0.00401	0.00407	+1.5
0.00126	0.00127	-0.8

The thickness of the layer of solution in these determinations was 10 cm. and the volume 50 ml

### III. Sources of Error in Color Methods

The errors peculiar<sup>21</sup> to the determination of substances by color methods are of three kinds:

1. Those having their origin in the system *constituent + reagent*  $\rightarrow$  *colored product*. These errors may be subdivided into those associated with:
  - a. The reproducibility of the color, and the closely related factor,
  - b. The stability of the color.

<sup>19</sup> G. Kortüm, *Angew. Chem.*, **50**, 193 (1937).

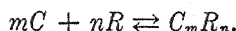
<sup>20</sup> H. von Halban and E. Zimpelmann, *Z. Elektrochem.*, **34**, 397 (1923).

<sup>21</sup> Naturally colorimetric methods are subject to other errors common to all quantitative methods, and sometimes these errors may have a large effect. For example, in an indirect colorimetric method in which a constituent is determined from the color given by another substance supposedly bearing a constant relation to the first such errors may determine the accuracy of the procedure. Thus in determining sodium colorimetrically, the metal must first be precipitated as the triple acetate (p. 404) and the uranium in the precipitate is then determined colorimetrically. The chief limitation of this method lies in the difficulty of obtaining the amount of uranium equivalent to the quantity of sodium because of incomplete precipitation of the triple acetate and solubility losses on washing.

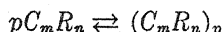


2. Those due to foreign substances, which may have a positive effect (giving a color of their own) or a negative one (reducing the color given by the constituent being determined).
3. Those involved in the measurement or comparison of the color intensity.

Errors of (3) have already been considered in sufficient detail for our purpose, but those of (1) and (2) require some discussion. The conditions in a color reaction for quantitative purposes must be capable of control so that virtually constant amounts of the colored product will be given by constant amounts of the constituent being determined. The reaction between the constituent and the reagent may in the simpler cases be represented by an equation of the general type:



Sometimes a further equilibrium of the type



may be involved, and moreover more than one colored species may be produced in the reaction. The latter appears to be the case in the reaction between cupric ions and ammonia, and possibly also in that between ferric ions and thiocyanate. It is desirable but not necessary that practically all of the constituent be converted into the colored product. If a standard curve is constructed all that is strictly necessary is the possibility of reproducing the color system without difficulty over a considerable range of concentrations of the constituent. If the reagent is used in large excess, as is generally the case, so that the quantity consumed in the reaction is small compared to that originally added,  $[R]^n$  is very nearly constant in the equilibrium expression

$$\frac{[C_mR_n]}{[C]^m[R]^n} = K,$$

and therefore  $\frac{[C_mR_n]}{[C]^m}$  is constant. If  $C$  and  $R$  are colorless, this means that the color intensity of the solution will be proportional to the total amount of the constituent present if  $m = 1$ , but not for other values, and Beer's law will be followed if there are no other disturbing factors.

The variables that may have to be controlled in a color reaction include the pH of the medium, the excess of the reagent, the time of standing before the color intensity is measured or compared, and the temperature required to develop the color. If these factors do not require too close control, the color should as rule be reproducible, provided that the colored product is stable.

The stability of the products of color reactions varies over a wide range. On the one hand we have substances such as permanganate and chromate which in a suitable environment show no change in solution for months or even years, and on the other hand certain organic products, illustrated by the evanescent substance formed when benzidine is oxidized by permanganate and other strong oxidizing agents, which decompose in a matter of minutes or seconds. As a rule organic reagents give less stable products than do the inorganic, but in many cases the organic product is sufficiently stable to enable it to be used for quantitative purposes to give results of high accuracy.

The natural tendency of many colored substances to be transformed with time into others which are colorless or less strongly colored may frequently be minimized or practically prevented if suitable precautions are taken. First of all, conditions of acidity, concentration of reagent, etc. may be found at which the stability of the product is a maximum. Light frequently hastens decomposition or produces it. For example, the ferric thiocyanate complex in aqueous solution is markedly sensitive to light; dithizone and the dithizonates in organic solvents decompose slowly on exposure to illumination. An increase in temperature may have an unfavorable effect on stability, especially if organic substances are involved. Solutions of dithizone and various dithizonates in carbon tetrachloride and chloroform may be kept for days without appreciable change if stored in an ice box, but may change quite rapidly at summer temperatures. Occasionally organic substances are fairly easily air-oxidized, and the stability of the color system is improved if a reducing environment can be maintained.

Instability is a characteristic of colloidal systems, and special attention must be paid to the time effect when the method involves the formation of a suspension of a slightly soluble substance (*cf.* p. 250).

Methods for avoiding to a greater or less extent the errors due to foreign substances are indicated in Table 7.

#### *Failure of Beer's Law<sup>22</sup>*

At this point we may consider briefly the reasons for the failure of Beer's law. In the first place, Beer's law as it is generally stated is actually the limiting case of a more exact relation

$$\log \frac{I_0}{I} = \frac{n}{(n^2 + 2)^2} kc$$

<sup>22</sup> The material in this section is based on a discussion by G. Kortüm and M. Seiler, *Angew. Chem.*, 52, 687 (1939).

in which  $n$  is the refractive index of the solution.<sup>23</sup> Ordinarily  $n$  changes so little from one concentration to another that the coefficient  $n/(n^2 + 2)^2$  may be disregarded.

A reason for true deviation of a color system from Beer's law lies in the interaction of the light-absorbing molecules or ions in the solution either with each other or with foreign substances ("neutral salt effect"). This leads to a change in the absorption curve. The effect is small, but by no means negligible, with most inorganic substances at low concentrations (cf. Table 6). Potassium dichromate shows greater deviations than do most salts. In trace analysis, in which very dilute solutions are usually being dealt with, serious error is not likely to arise from the operation of this effect. The effect of neutral salts may be more serious, since it is not unusual for the sample solution to contain a comparatively high concentration of some salt, or perhaps base or, less often, acid.

TABLE 6  
ILLUSTRATIONS OF DEVIATIONS FROM BEER'S LAW<sup>a</sup>

K <sub>2</sub> CrO <sub>4</sub> in 0.005 N NaOH at 366 mμ		K <sub>2</sub> CrO <sub>4</sub> in 0.005 N NaOH at 436 mμ		K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> in 0.005 N H <sub>2</sub> SO <sub>4</sub> at 366 mμ	
C (moles/liter)	ε	C (moles/liter)	ε	C (moles/liter)	ε
1.38 × 10 <sup>-4</sup>	4609	6.8 × 10 <sup>-4</sup>	320.0	2.38 × 10 <sup>-5</sup>	2581.6
4.92 × 10 <sup>-4</sup>	4608	1.87 × 10 <sup>-3</sup>	319.75	8.50 × 10 <sup>-5</sup>	2596.2
2.66 × 10 <sup>-3</sup>	4617	3.7 × 10 <sup>-3</sup>	319.5	2.25 × 10 <sup>-4</sup>	2629.9
		6.8 × 10 <sup>-3</sup>	319.15	4.59 × 10 <sup>-4</sup>	2687.1
		3.7 × 10 <sup>-2</sup>	317.55	8.04 × 10 <sup>-4</sup>	2751.2
				4.35 × 10 <sup>-3</sup>	3172.4

<sup>a</sup> From G. Kortüm, *Z. physik. Chem.*, 33B, 243 (1936).

Apparent failure of Beer's law may result when the color system involves an equilibrium between the constituent, reagent, and the colored product, as we have just seen. Deviations from this cause can not justly be included under failure of Beer's law, because this law simply states that the extinction is proportional to the concentration of the colored substance; it does not state that the extinction must be proportional to the analytical concentration of the constituent which forms the colored substance. The apparent failure of Beer's law when light of insufficient monochromaticity is used has already been considered and nothing more need be said about it here.

#### IV. Desiderata for Color Reactions for Trace Analysis

These may be summarized as follows:

##### 1. High Sensitivity

This is the most important desideratum when minute amounts of substances are to be determined. Reproducibility and stability of the colored

<sup>23</sup> G. Kortüm, *Das optische Verhalten gelöster Elektrolyte*. Enke, Stuttgart, 1936; p. 65.

TABLE 7

## GENERAL METHODS FOR THE PREVENTION OR THE MINIMIZATION OF ERRORS DUE TO FOREIGN SUBSTANCES IN COLORIMETRIC ANALYSIS

Type of Interference	Procedure	Remarks
<b>I. Positive</b> A. The foreign substance is colored but undergoes no change on addition of reagent	1. Measure the transmittancy of the solution at a wave length at which the foreign substance shows practically no absorption, but at which the compound of the constituent absorbs strongly, or use method IB (1).	This procedure often successful.
	2. Measure the transmittancy of the solution before and after the addition of reagent.	The most generally applicable procedure.
	3. Measure the transmittancy of the solution after the addition of reagent against the original solution in the reference cell (both solutions at the same concentration), calling the transmittancy of the latter 100 per cent.	A variant of the preceding procedure. Used in preference to others when sufficient sample solution is available.
	4. Add a reagent (usually a complex-forming agent) to destroy the color of the foreign substance.	A useful procedure in both spectrophotometric and colorimetric methods.
	5. After the transmittancy of the sample solution containing reagent has been measured, add a reagent which will discharge the color without affecting that of the foreign substance, and determine the transmittancy of the resulting solution.	In the determination of manganese as permanganate in the presence of iron, hydrogen peroxide may be used to destroy the permanganate.
	6. Add a solution of the foreign substance to the standards to duplicate the color of the sample before reagent is added.	For colorimetry by the series and colorimetric titration methods.
	7. Extract the colored compound of the constituent being determined by the use of an immiscible solvent and measure the transmittancy of the latter.	Example: determination of cobalt in the presence of nickel by extraction of cobalt thiocyanate complex with amyl alcohol.
B. The foreign substance may or may not be colored, but it gives a colored product with the reagent.	1. Measure the transmittancy at two suitable wave lengths and calculate the concentration of the constituent, using two simultaneous equations involving the known extinction coefficients of the two colored substances, or use method IA (1).	Accuracy may not be great, especially when the foreign substance preponderates or gives a strongly colored compound. For an example, see p. 121
	2. Convert the interfering substance into a non-reactant by (a) complex formation, or (b) oxidation or reduction.	A powerful method, convenient to use, which is frequently applicable.
	3. Make separations, preferably employing a method which effects a direct isolation of the constituent to be determined.	The method which is applied when others fail; applicable to most constituents; must be resorted to when minute traces are to be determined. See Chapter II.

TABLE 7—(Continued)

Type of Interference	Procedure	Remarks
<b>II. Negative</b> The foreign substance prevents or hinders the reaction between the constituent and reagent, thus reducing the color intensity. The interference may be due to the formation of a complex between the substance and the constituent or the reagent, destruction of the reagent, etc.	<ol style="list-style-type: none"> <li>1. Increase the excess of reagent.</li> <li>2. Find the extinction, <math>E_x</math>, given by <math>x</math> g. of constituent in <math>V</math> ml. of solution. Add <math>a</math> g. of the constituent in a volume of <math>v</math> ml. and obtain the extinction <math>E_{x+a}</math> of the mixture (<math>a</math> should be comparable in amount to <math>x</math> and <math>v</math> should be small). If there are no complications, we have the relation               <math display="block">\frac{E_x}{E_{x+a}} = \frac{x/V}{x+a}</math>               and               <math display="block">x = aV \frac{E_x}{E_{x+a}} \bigg/ \left( V + v - V \frac{E_x}{E_{x+a}} \right).</math> </li> <li>3. Prepare a standard solution having the same composition as the sample solution.</li> <li>4. As in IB 2.</li> <li>5. Separate the constituent.</li> </ol>	<p>Of limited value. Helpful when the interfering substance forms a relatively weak complex with the constituent. Thus a large excess of thiocyanate reduces the error due to phosphate in the determination of ferric iron.</p> <p>This method is not often applied but it can be used with profit in checking the results obtained with solutions of unknown composition to avoid gross errors.</p> <p>Occasionally applicable, as for example in the determination of trace constituents in sea water or chemical reagents, or other samples having a known composition.</p>

product can be sacrificed within limits to obtain sensitivity. It is better to be able to determine a minute amount of a constituent with an error of 25 per cent than not to be able to determine it at all. With a fixed minute quantity of substance the accuracy obtainable is directly proportional to the sensitivity of the reaction employed, other things being the same.

## 2. Specificity or Selectivity

Few if any reagents are strictly specific (reacting only with one substance) but they differ among themselves in the number of substances with which they will give a more or less sensitive reaction, a property which is described by the term *selectivity*. Strictly one should speak of the specificity or the selectivity of a reaction rather than of a reagent. Dithizone for example will react with nearly a score of metals, but by adjustment of the pH of the medium and the use of complex-forming agents it can be made to yield

practically specific reactions for a number of metals. Although lack of selectivity does not necessarily exclude a reagent from use in trace analysis, selectivity is nevertheless a desirable property, for it generally permits a determination to be made with the expenditure of less time and effort.

### 3. Good Reproducibility and Stability of the Color

#### 4. Adherence to Beer's Law

This is the least important of the desiderata, but a desirable one nonetheless. A system following Beer's law is more convenient to use and permits greater accuracy than one which does not, other factors being comparable. As a matter of fact it is a little superfluous to specify that a color system should obey Beer's law, for in the natural state of things it generally does so within close limits if the colored substance is soluble. Even when the colored substance is slightly soluble and a colloidal dispersion is obtained, color intensity is proportional to concentration in many cases; systems involving lakes are an exception (see p. 70). As pointed out above, the phrase "adherence to Beer's law" is frequently used, not in the strictly correct sense, but to signify proportionality between color intensity and analytical concentration of the substance being determined.

### *Organic Reagents*

Colorimetric trace analysis would be sadly hampered without organic reagents. The property shown by many organic compounds of forming strongly colored internal complexes with metals is put to good use in colorimetric analysis, being especially valuable when minute quantities of metals are to be determined. Frequently organic reagents show good selectivity, which under the proper conditions can be made the basis of reactions having actual or virtual specificity.<sup>24</sup> The vast array of organic compounds and the ease with which a given compound can often be modified by the introduction of various groups to alter the solubility, color, etc. permit the hope that the number of useful organic reagents will be materially increased in the future.

From the standpoint of trace analysis, an important property of many of the metal-organic complexes is their extractability by organic solvents not miscible with water to give solutions that are more or less strongly colored.<sup>25</sup> Traces of metals can thus be isolated and separated from large

<sup>24</sup> For a discussion of atomic "specific" groupings in organic compounds see F. Feigl, *Specific and Special Reactions*, (translated by R. E. Oesper). Nordeman, New York, 1940; *Qualitative Analysis by Spot Tests*. Nordeman, New York, 1939.

<sup>25</sup> A small number of inorganic compounds of strong color are extracted by certain organic solvents. Among these may be mentioned chloroplatinous acid, iodobismuthous acid and "molybdenum blue."

amounts of other substances in many cases, and sometimes determined by the color of the organic solvent.

There are a few organic reagents which are important because they yield strongly fluorescent metal complexes, some of which can be extracted by immiscible solvents.

Although organic reagents play an important role in trace analysis, they do not monopolize the field, and a number of inorganic reagents or determination forms are the basis of some sensitive and reliable trace methods for metals, for example, manganese as permanganate, chromium as chromate, titanium with hydrogen peroxide, vanadium with peroxide or phosphotungstic acid, arsenic and other metals by the formation of molybdenum blue, bismuth and platinum with iodide, gold and tellurium as the colloidal metals, etc.

### V. Fluorimetry

There are a number of elements that can be determined with greater sensitivity and specificity by fluorimetric than by colorimetric methods, and the trace analyst should be familiar with the possibilities of fluorescence analysis. Only a brief outline of the subject will be given here.<sup>26</sup>

The concentration of a fluorescent substance in a solution is obtained by illuminating the latter with ultraviolet radiation and comparing or measuring the intensity of the light emitted. The intensity of the fluorescence is a function of a number of factors:

$$F = AI_0 (1 - 10^{-kcl})$$

where  $F$  = fluorescence intensity,

$I_0$  = intensity of the incident radiation,

$A$  = fraction of radiation absorbed,

$k$  = a constant depending on the particular substance, solvent, wave length, etc.,

$c$  = concentration of the fluorescing substance,

$l$  = depth of the layer of solution.

If  $kcl$  is small, say less than 0.01, the above expression becomes

$$F = 2.3 AI_0 kcl$$

<sup>26</sup> The following works may be consulted for further information on fluorescence analysis, including more or less material on quantitative methods: M. Haitinger, *Die Fluoreszenzanalyse in der Mikrochemie*. E. Haim, Vienna and Leipzig, 1937. P. W. Danckwortt and J. Eisenbrand, *Lumineszenzanalyse im filtrierten ultravioletten Licht*. 4th ed., Akademische Verlagsgesellschaft, Leipzig, 1940. J. A. Radley and J. Grant, *Fluorescence Analysis in Ultraviolet Light*. 3d ed., Van Nostrand, 1939. For a review of fluorescence analysis see C. E. White, *Ind. Eng. Chem., Anal. Ed.*, **11**, 63 (1939).

and  $F$  is then directly proportional to the concentration. The linear relation is usually found to hold in practice over a considerable range of concentrations; at higher concentrations a plot of  $F$  against  $c$  curves toward the  $c$ -axis.<sup>27</sup> It should be pointed out that a solution of a fluorescing substance shows maximum fluorescence at a certain concentration, above which the fluorescence decreases. Care should be taken to work with solutions whose concentrations lie below those near the flat maximum of the intensity-concentration curve.

Comparison or measurement of the fluorescence intensity of solutions may be made with a modified Duboscq colorimeter<sup>28</sup> or a Pulfrich photometer,<sup>29</sup> but more precise measurements can be

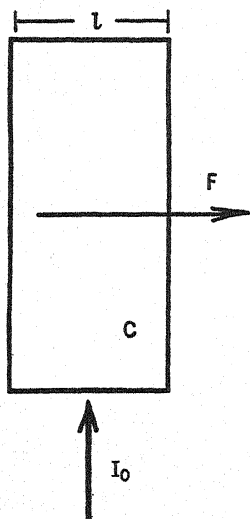


Fig. 12.—Illustrating the principle of fluorescence measurements in solutions.

be made with properly designed instruments in which a photoelectric cell and galvanometer are employed to obtain the intensity of the emitted light. Such fluorophotometers may have either one or two photocells.<sup>30</sup> The essential features of two typical instruments are schematically represented in Fig. 13. A filter is used to isolate the desired wave lengths from the ultraviolet source. By the proper choice of exciting wave length it is sometimes possible to prevent the fluorescence of other substances in the solution. For the greatest fluorescence intensity the wave length of the ultraviolet radiation should be close to the wave length of maximum absorption shown by the solution. Another filter is placed in front of the photocell to absorb reflected or scattered ultraviolet light (a small amount of suspended material in the solution will then be without effect). In some instances the determination of a fluores-

cent substance may be made more specific by using a photocell filter which will largely absorb the fluorescent light emitted by a foreign substance in

<sup>27</sup> Cf. F. Kavanagh, *Ind. Eng. Chem., Anal. Ed.*, **13**, 108 (1941).

<sup>28</sup> B. Josephy, *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, **4**, 46 (1934).

<sup>29</sup> See, for example, C. E. White, and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.*, **12**, 229 (1940).

<sup>30</sup> For descriptions of one-cell instruments consult the papers of F. H. Cohen, *Rec. trav. chim.*, **54**, 133 (1935); D. B. Hand, *Ind. Eng. Chem., Anal. Ed.*, **11**, 306 (1939). A double-cell fluorophotometer has been described by F. Kavanagh, *Ind. Eng. Chem., Anal. Ed.*, **13**, 108 (1941). See also R. H. Müller, *ibid.*, **13**, 714 (1941). A description of an alternating current-operated fluorimeter with vacuum photocells is given by R. P. Krebs and H. J. Kersten, *ibid.*, **15**, 132 (1943).



the solution. The fluorescence intensity of the unknown solution is referred to that of a comparison solution containing a stable fluorescing substance in suitable concentration. A solution of quinine sulfate or fluorescein is often used for this purpose. The concentration of the fluores-

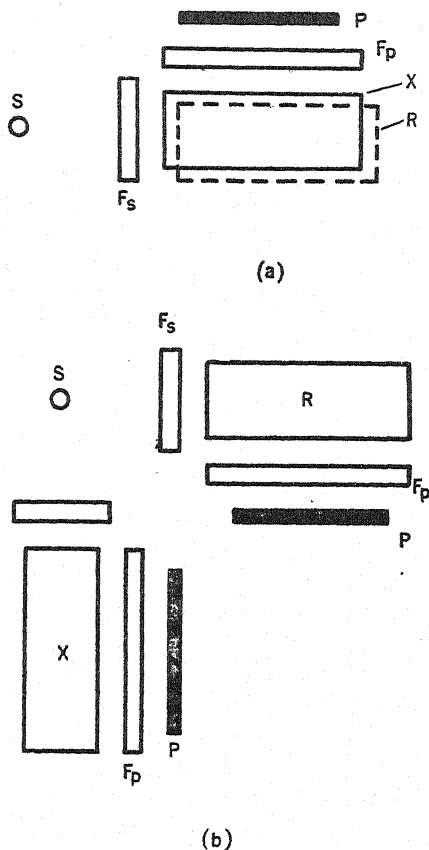


Fig. 13.—Schematic representation of measurement of fluorescence of solutions with (a) single photocell (b) double photocell.  $S$  = source of ultraviolet,  $P$  = photocell,  $X$  = cell holding sample solution,  $R$  = cell holding reference solution,  $F_s$  = filter for ultraviolet,  $F_p$  = filter for photocell.

cent substance is obtained by reference to a standard curve in which the concentration is plotted against the fluorescence intensity.

Fluorimetry by visual comparison is less exact than fluorophotometry, but nevertheless is capable of giving useful results. As a matter of fact visual comparison offers an advantage over the use of a fluorophotometer when the absolute amount of the fluorescing substance is very minute,

since volumes of 1 ml. or less can be used in the former method whereas such volumes are not great enough for ordinary fluorophotometer cells. For the determination of such elements as beryllium, aluminum, and gallium by methods which are described elsewhere in this book, the ultraviolet source need not be particularly strong. A Westinghouse type G-5 mercury glow lamp with a purple Corex shell may be mentioned as one satisfactory source of ultraviolet radiation in visual work. It provides a relatively large area of radiation. In carrying out a comparison the tubes (p. 42) or vials containing the sample solution and one of the standard solutions are held vertically in juxtaposition close above the lamp. The tubes should be interchanged before deciding which shows the stronger fluorescence, in order to avoid error due to non-uniform radiation. Differences of 10 per cent in fluorescence intensity can be distinguished in the optimum concentration range (*cf.* p. 42). The use of solutions giving too strong a fluorescence must be avoided, for then a concentration difference of 10 per cent and greater will be undetectable because of the imperceptible difference in fluorescence of two such solutions. The beginning of the optimum concentration range may be taken to lie at 10 times the concentration giving the minimum visible fluorescence.

The visual sensitivity of a fluorescence reaction can be described in the same manner as colorimetric sensitivity by stating the smallest quantity ( $\gamma$ ) of the element in a column of solution of unit cross section (1 cm.<sup>2</sup>), in the direction of view, which suffices to give a perceptible fluorescence, or a fluorescence just perceptibly stronger than that of a blank. The conditions of observation, particularly the intensity and the wave length of the ultraviolet radiation, must naturally be specified. In some instances the intensity of the ultraviolet excitation is of subsidiary importance, because the blank may already give an appreciable fluorescence, due either to the solvent (organic liquids such as chloroform, alcohol, and acetone commonly show a weak fluorescence) or the reagent. Since the solvent may fluoresce, the fluorescence sensitivity unlike color sensitivity may not be independent of the depth of solution layer examined. Practically this limitation is of slight importance since the depth of layer examined is usually not greater than 1 or 2 cm. An example of the great sensitivity of fluorescence reactions is provided by the beryllium-morin reaction in slightly basic solution, whose sensitivity is approximately 0.002  $\gamma$  Be per cm.<sup>2</sup> in ultraviolet light. This sensitivity is roughly one hundred times that of the more sensitive color reactions. Not all fluorescence reactions have such great sensitivity however. The sensitivity of the gallium-hydroxyquinoline reaction in which the gallium complex is extracted from an aqueous solution of pH 3.0 by chloroform and the latter examined in ultraviolet light is about 0.1  $\gamma$  Ga per cm.<sup>2</sup> Since 1 ml. of chloroform suffices for the extraction of 10-20

ml. of solution the concentration limit of this test is  $1:10^8$ . The photometric sensitivity of fluorescence methods (analogous to the spectrophotometric sensitivity of colorimetry discussed on p. 40) depends upon the reproducibility of the measurements. Data on this point so far as inorganic fluorimetry is concerned are lacking.

The errors encountered in fluorimetry are to a great extent the analogues of the errors associated with colorimetry but some are peculiar to fluorescence phenomena. Foreign substances may have a profound effect on the fluorescence intensity of a substance. They may diminish the fluorescence by absorbing the ultraviolet radiation (chromate ion is an example), by absorbing the emitted light and by direct action (quenching). On the other hand the foreign substance may itself fluoresce. Not infrequently it is found that the fluorescent substance is rapidly destroyed by ultraviolet light, and the fluorescence intensity must then be determined quickly or successive readings extrapolated to zero time.

## VI. Turbidimetry and Nephelometry

These methods are used more by necessity than by choice. In turbidimetry the amount of light absorbed by a suspension is determined, and in nephelometry the amount scattered by the suspension is determined. A colorimeter or photometer may be used in turbidimetric comparisons or measurements. On the other hand, a nephelometer does not differ in any essential respect from a fluorimeter except in the character of the illumination. Since nephelometry is rarely used in inorganic trace analysis at the present time, a description of nephelometers will be omitted here.<sup>31</sup>

The chief difficulty in turbidimetry and nephelometry lies in obtaining reproducible suspensions. Small variations in the manner of addition of the precipitant, in the temperature, and in the time elapsing before observation may have a great effect on the light absorption or scattering, because of the effect of these factors on the primary or secondary particle size of the precipitate. Moreover, electrolytes may exert a profound effect. Slightly soluble substances differ greatly in their suitability for use in turbidimetry and nephelometry. It is desirable that the precipitate be exceedingly slightly soluble, that it form rapidly, and that it be colored or opaque (the latter desiderata for turbidimetry). It is often found that the optical density of the suspension varies linearly with the concentration of the suspended substance over a wide range, particularly if the substance absorbs strongly. The relation fails at very low concentrations. Colloidal tellurium produced by precipitation with stannous chloride, colloidal gold (p. 251), silver diethylaminobenzylidenerhodanine, copper ferrocyanide, and

<sup>31</sup> See J. H. Yoe, *Photometric Chemical Analysis*, Vol. II. Wiley, New York, 1928.

many heavy metal sulfide dispersions show the linear relation. Silver chloride suspensions give a more complex extinction-concentration curve (p. 402). In colorimetric determinations based on lake formation, in which the reagent (dye) is adsorbed on the surface of the precipitate with a change in color, it is frequently found that there is practically a linear relation between extinction and concentration at low concentrations. This is to be expected, since when the reagent is in large excess the surface of the precipitate becomes saturated with it, and over a limited range the color intensity is proportional to the concentration of the colloidal precipitate. When the ratio of reagent to precipitate decreases below a more or less fixed value the amount of dye adsorbed begins to decrease markedly and the extinction-

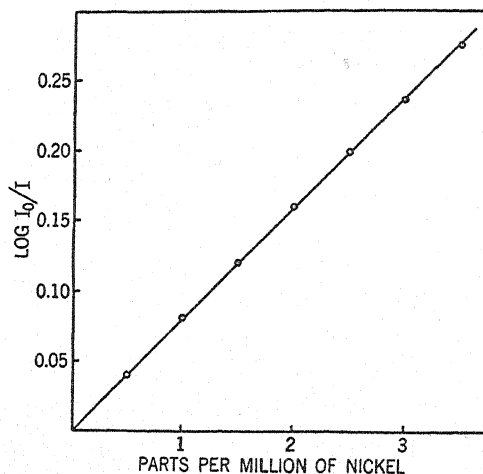


Fig. 14.—Determination of nickel as colloidal nickel dimethylglyoxime in the presence of gelatin (from data of Juza and Langheim, *loc. cit.*).

concentration curve then tends to run parallel to the concentration axis. See, for example, p. 307.

Colorless suspensions are of minor value in trace analysis because of the low sensitivity afforded by them. In other words it is the light absorbing power rather than light scattering ability of a suspension that determines its value for use in analysis. Colored or opaque dispersions of slightly soluble substances have been made the basis of sensitive trace methods (Fig. 14).<sup>32</sup> A protective colloid such as gelatin is frequently added to obtain a more stable dispersion of the colloidal substance. If the concentration of the precipitated substance is low, however, such addition may be omitted. Sometimes it is difficult to distinguish between a true colorimetric

<sup>32</sup> See R. Juza and R. Langheim, *Angew. Chem.*, 50, 255 (1937) for some examples of colorimetry with colloidal solutions.

and a turbidimetric method. For example, the lakes given by alizarin and other hydroxyanthraquinones may under some conditions be so finely dispersed that they are practically molecular. The time factor is important in all determinations involving the use of a suspension and readings must often be made a definite time after the addition of the precipitant.

It may be pointed out that turbidimetric, as well as colorimetric, measurements at high light transmittancies have an inherent weakness which decreases precision: the amount of light scattered or absorbed by the substance being determined must be found as the difference between the intensities of two light beams. Nephelometric (and fluorimetric) intensity measurements do not suffer from this limitation and therefore present the possibility of greater sensitivity and precision. Of course other factors may prevent the exploitation of this advantage.

## CHAPTER IV

### GENERAL COLORIMETRIC REAGENTS

In this chapter some colorimetric reagents that can be used for the determination of more than one element are considered. Dithizone is the general heavy metal reagent par excellence and its importance in trace analysis calls for a fairly full discussion of its properties and use. Other reagents are discussed more briefly.<sup>1</sup>

#### I. Dithizone

Diphenylthiocarbazone, or dithizone,  $\text{S}=\text{C} \begin{cases} \text{NH} \cdot \text{NH} \cdot \text{C}_6\text{H}_5 \\ \text{N}=\text{N} \cdot \text{C}_6\text{H}_5 \end{cases}$  was first

prepared by Emil Fischer,<sup>2</sup> who noted the reaction of the compound with heavy metals to give brilliantly colored products. No analytical use was made of the compound until 1925 when Hellmut Fischer<sup>3</sup> showed its great value for the detection and determination of various heavy metals. In an extensive series of papers,<sup>4</sup> H. Fischer and his coworkers have given procedures for the detection and determination of traces of many heavy metals with dithizone. The reagent has proven highly valuable and there is now an extensive literature concerning its use. Although dithizone has been applied chiefly in the determination of traces of lead, it is no less valuable for the determination of small amounts of other metals. Without it the determination of traces of zinc and cadmium in complex materials would be virtually impossible. The sensitivity of dithizone methods approaches

<sup>1</sup> The following books on organic reagents contain more or less information on the use of organic compounds for qualitative and quantitative color reactions: F. Feigl, *Qualitative Analysis by Spot Tests*, (translated by J. Matthews). Nordeman, New York, 1939; F. Feigl, *Specific and Special Reactions*, (translated by R. E. Oesper). Nordeman, New York, 1940. C. J. van Nieuwenburg, W. Böttger, F. Feigl, A. S. Komarovskiy, and N. Strafford, *Tables of Reagents for Inorganic Analysis*. Akademische Verlagsgesellschaft, Leipzig, 1938; J. H. Yoe and L. A. Sarver, *Organic Analytical Reagents*. Wiley, New York, 1941; I. Mellan, *Organic Reagents in Inorganic Analysis*. Blakiston, Philadelphia, 1941; W. Proding, *Organic Reagents Used in Quantitative Inorganic Analysis*, (translated by S. Holmes). Elsevier, New York, 1940. P. Von Stein, *Organic Reagents in Inorganic Analysis*. Chemical Publ. Co., Brooklyn, 1942. Research staff of Hopkin and Williams, *Organic Reagents for Metals and for Certain Acid Radicals*. Hopkin and Williams, London, 1943.

<sup>2</sup> E. Fischer, *Ann.*, **190**, 118 (1878); E. Fischer and E. Besthorn, *ibid.*, **212**, 316 (1882).

<sup>3</sup> H. Fischer, *Wiss. Veröffentl. Siemens-Konzern*, **4**, 158 (1925).

<sup>4</sup> For a review see H. Fischer, *Angew. Chem.*, **47**, 685 (1934); **50**, 919 (1937).

or equals that of spectrographic methods. Dithizone is also useful for the isolation of traces of heavy metals (*e.g.*, cobalt) which finally may be determined with another reagent.

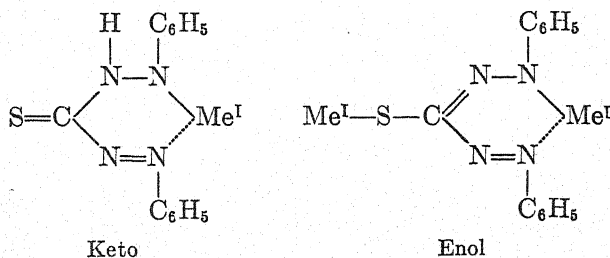
Dithizone is a violet-black solid which dissolves in most organic solvents to a greater or less extent. In hydrocarbons it is only slightly soluble. It dissolves readily in chloroform, and less readily in carbon tetrachloride. These two solvents are used exclusively in the preparation of dithizone solutions for analytical purposes. Dilute solutions of dithizone in carbon tetrachloride and chloroform are green, but more concentrated ones are dichroic (red in transmitted light, green in reflected light). In strongly polar solvents, such as nitrobenzene, dithizone is yellow.

When a solution of dithizone in an immiscible organic liquid is shaken with an aqueous solution of a reacting heavy metal, an internal complex salt—dithizonate—is formed, which generally is soluble in the organic solvent, to which it imparts a violet, red, orange or yellow color, depending upon the metal involved. Dithizone and the dithizonates are virtually insoluble in neutral and acid aqueous solutions<sup>5</sup> (but some dithizonates are decomposed when their carbon tetrachloride or chloroform solutions are shaken with dilute acid). In basic solutions dithizone dissolves with a yellow color to give the alkali metal dithizonate.

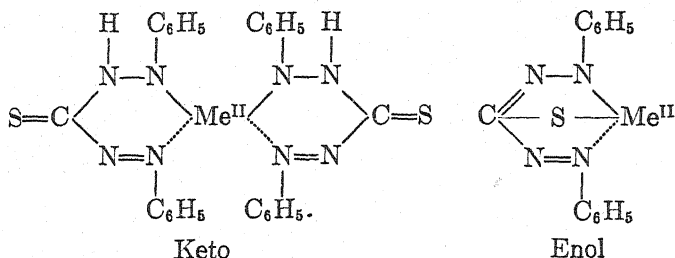
The dithizonates, like dithizone itself, are more soluble in chloroform than in carbon tetrachloride and still more soluble in strongly polar organic solvents.

### 1. The Metal Dithizonates

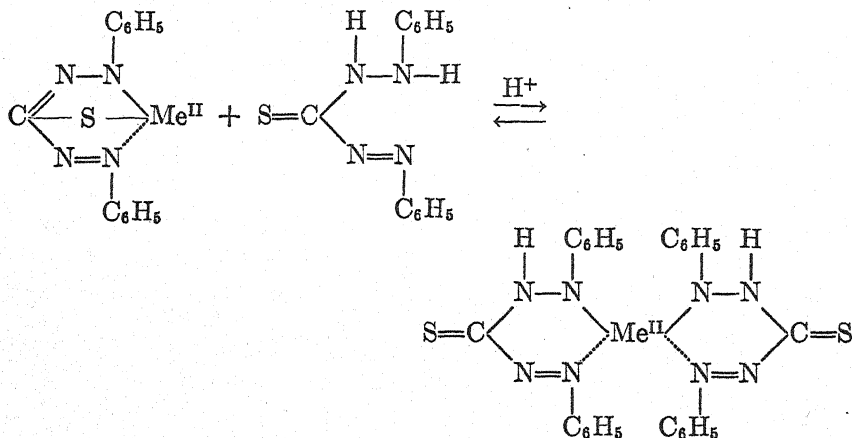
Some dithizonates can exist in two tautomeric forms, namely the keto and the enol. In the keto form, the hydrogen of the imide group of dithizone is replaced by the metal, and in the enol form the hydrogen of the sulfhydryl group of the hypothetical enol dithizone is also replaced, so that the enol form contains twice as much metal as the corresponding keto form. The formulas for the keto and enol forms of univalent and divalent metal dithizonates are given below:



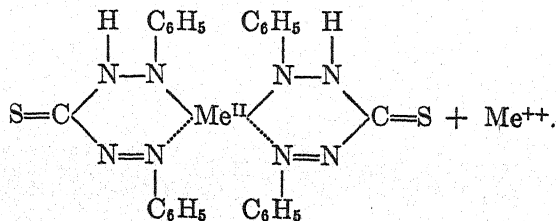
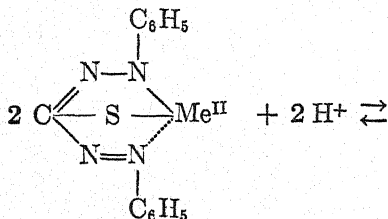
<sup>5</sup> When a carbon tetrachloride solution of dithizone is shaken with concentrated hydrochloric acid, dithizone partially passes into the acid layer and imparts a violet-red color to it. In 6 *N* hydrochloric acid dithizone is insoluble.



According to H. Fischer the keto forms of all the metal dithizonates exist; the enol forms of many metal complexes are not known. Copper, silver, and mercury readily form both keto and enol complexes. The keto tautomer is preferentially formed in acid or neutral solution, and the enol in basic solution or with a deficiency of dithizone. The enol form can be transformed into the keto by treatment with acid and dithizone:



or by the action of acid alone:





On the other hand, the keto tautomer can be transformed more or less easily into the enol tautomer (if this form exists) by the action of alkalies.

In Table 8 the metals forming complexes with dithizone are indicated, and in Table 9 some data regarding the metal dithizonates are given. It will be noted that certain metals react only in one valence. Thus  $\text{Fe}^{\text{II}}$ ,  $\text{Sn}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$  react, but not  $\text{Fe}^{\text{III}}$ ,  $\text{Sn}^{\text{IV}}$  and  $\text{Pt}^{\text{IV}}$ .

## 2. Metal-Dithizone Equilibria

The reversible<sup>6</sup> reaction between a metal ion and dithizone in acid medium can be represented by the general equation

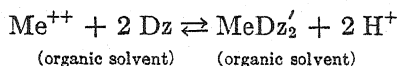


TABLE 8  
METALS REACTING WITH DITHIZONE  
(The enclosed elements yield dithizonates)

H																				
Li	Be															B	C	N	O	F
Na	Mg															Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br				
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—				
—	Ra	Ac	Th	Pa	U															

in which  $\text{Dz}$  = dithizone and  $\text{MeDz}_2'$  = keto dithizonate. On the basis of this equation it is a simple matter to derive an expression for the extractability of a metal as a function of the  $p\text{H}$  of the aqueous solution and the concentration of dithizone.<sup>7</sup> If the  $p\text{H}$  range is such that the metal is present as an aquo ion ( $\text{Me}^{++}$ ) and dithizone and dithizonate are present in non-associated forms, the following relation exists:

$$\frac{[\text{MeDz}_2']_o}{[\text{Me}^{++}]_w} = K \frac{[\text{Dz}]_o^2}{[\text{H}^+]_w^2} \quad (1)$$

<sup>6</sup> Not all metal—dithizone reactions are simply reversible. Thus cobalt and nickel do not react markedly with dithizone in dilute acid medium (*e.g.*,  $p\text{H}$  2), but if either dithizonate has once been formed (in basic solution) it is not readily decomposed by dilute acids. The behavior of cobalt and nickel dithizonates in this respect is similar to the behavior of the sulfides. Cobalt dithizonate is more stable than nickel dithizonate to the action of acids.

<sup>7</sup> I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.*, **63**, 1906 (1941).

TABLE 9  
 THE DITHIZONATES<sup>a</sup>
 $K$  = keto     $E$  = enol     $S$  = soluble     $I$  = insoluble

Metal	Complex	Color (CCl <sub>4</sub> )	Solubility in CCl <sub>4</sub> or CHCl <sub>3</sub>	pH for extraction	Remarks
Bismuth	$K$	Orange-yellow	$S$	>2 (CCl <sub>4</sub> )	See Reith and van Dijk, <i>Chem. Weekblad</i> , 36, 343 (1939). Also reacts in presence of KCN (pH 7-8).
	$E$	Orange-red	$S$	Basic soln.	
Cadmium	$K$	Red	$S$	Basic soln.	Stable when shaken with 1 $N$ NaOH
Cobalt	$K$	Violet	$S$	7-9 (optimum in CCl <sub>4</sub> )	Organic soln. of dithizonate quite stable to dilute mineral acids.
	$E?$	Brownish	$S$	Strongly basic soln.	May be decomposition product.
Copper (I)	$K$	Violet	$S$	Dil. mineral acid soln. (ca. 0.1 $N$ )	Only slightly soluble in CCl <sub>4</sub> .
	$E$	Red-brown	$S$	Basic soln.	
	(II) $K$	Violet-red	$S$	Dil. mineral acid soln.	
	(II) $E$	Yellow-brown	$S$	Basic soln.	
Gold		Yellow	$S(\text{CHCl}_3)$	Dil. mineral acid soln.	Can also be formed in slightly acid soln. when copper is in excess of Dz.
					Red color first appears on shaking; this quickly changes to orange and then to yellow. Floes in CCl <sub>4</sub> . Au (III) probably reduced to Au (I).
Indium		Red	$S$	5-6 (CCl <sub>4</sub> )	pH adjustment critical. Also reacts in presence of cyanide at pH 5-6.
Iron (II)		Violet-red	$S$	6-7 (CCl <sub>4</sub> )	Fe (III) does not form a complex but oxidizes Dz in basic medium, especially in presence of cyanide.
Lead	$K$	Cinnabar red	$S$	8.5-11 (optimum in CHCl <sub>3</sub> )	Solution very unstable. Brown floes in CCl <sub>4</sub> .
Manganese		Violet-brown (CHCl <sub>3</sub> )	$S(\text{CHCl}_3)$	ca. 11	
Mercury (I)	$K$	Orange	$S$	Dil. mineral acid soln.	Can also be formed in weakly alkaline solution with an excess of Dz.
	$E$	Purplish red	$S$	Basic medium	
	(II) $K$	Orange-yellow	$S$	Dil. mineral acid soln.	
	(II) $E$	Purplish red	$S$	Basic medium	
Nickel		Brownish	$S$	Weakly basic medium	CCl <sub>4</sub> solution not easily decomposed by dilute mineral acids. From a strongly basic solution, CCl <sub>4</sub> extract is gray.

<sup>a</sup> Based on data of H. Fischer and others, and upon the writer's observations.

TABLE 9—(Continued)

Metal	Complex	Color (CCl <sub>4</sub> )	Solubility in CCl <sub>4</sub> or CHCl <sub>3</sub>	pH for extraction	Remarks
Palladium	<i>E</i> ?	Brown-red (CHCl <sub>3</sub> )	<i>S</i> (CHCl <sub>3</sub> )	Dil. mineral acid soln.	Partly soluble in CCl <sub>4</sub> (dark violet). Reaction is slow.
	<i>K</i>	Brownish-green (CHCl <sub>3</sub> )	<i>S</i> (CHCl <sub>3</sub> )		By addition of Dz to solution of enol compound. Stable towards 6 <i>N</i> NaOH and 6 <i>N</i> H <sub>2</sub> SO <sub>4</sub> .
Platinum (II)		Violet or violet-red aqueous layer; green CCl <sub>4</sub>		Weakly acid solution	Probably a colloidal solution; sometimes violet flocs are obtained (insoluble in CHCl <sub>3</sub> ). Pt (IV) does not react; neither do other Pt metals in quadrivalent or trivalent state.
Silver	<i>K</i>	Yellow	<i>S</i>	Dil. mineral acid soln.	
	<i>E</i>	Red-violet	<i>I</i>	Basic soln.	Slightly soluble in CHCl <sub>3</sub> (red solution).
Thallium (I)	<i>K</i> ?	Red	<i>S</i>	9-12 (CCl <sub>4</sub> )	Also formed in presence of cyanide.
(III)	<i>K</i> ?	Yellowish red	<i>S</i>	3-4 (CCl <sub>4</sub> )	Reaction not complete. Tl (III) also oxidizes Dz.
Tin (II)	<i>K</i>	Red	<i>S</i>	> 4 (optimum 6-9 in CCl <sub>4</sub> )	Not stable
Zinc	<i>K</i>	Purplish red	<i>S</i>	Neutral or weakly basic soln.	With an excess of Dz extraction can be made complete in weakly acid medium.

in which *o* and *w* indicate the immiscible organic solvent phase and aqueous solution respectively. Strictly, activities should be written instead of concentrations, and the more exact expression is

$$\frac{[\text{MeDz}'_2]_o}{[\text{Me}^{++}]_w} = K \frac{[\text{Dz}]_o f_{\text{Me}^{++}}}{[\text{H}^+]_w^2 f_{\text{H}^+}^2} \quad (2)$$

in which  $f_{\text{Me}^{++}}$  and  $f_{\text{H}^+}$  are the activity coefficients of the metal and hydrogen ions. Equation (1) has been tested in a preliminary way for zinc with a chloroform solution of dithizone. The ratio  $\frac{[\text{ZnDz}'_2]_{\text{CHCl}_3}}{[\text{Zn}^{++}]_{\text{H}_2\text{O}}}$  was varied from 0.3 to 27 at pH 3.97 and  $K$  was found to remain sensibly constant and equal to 3.2. At pH 3.05 the value of  $K$  was found to be 4.5 (the activity coefficient of the zinc ions was not taken into account). It is worth noting that a pH change of one unit alters the value of the ratio  $\frac{[\text{MeDz}'_2]_o}{[\text{Me}^{++}]_w}$  one hundred fold.

If the pH of the aqueous solution is such that the metal ion is more or

less completely hydrolyzed, the expression for the extractability of the metal becomes

$$\frac{[\text{MeDz}'_2]_o}{[\text{Me}]_w} = K \frac{[\text{Dz}]_o^2}{\{[\text{H}^+]_w^2 + K_{1\text{hyd.}}[\text{H}^+]_w + K_{2\text{hyd.}}\}}$$

where  $[\text{Me}]_w = [\text{Me}^{++}] + [\text{MeOH}^+] + [\text{Me}(\text{OH})_2]$

$$K_{1\text{hyd.}} = \frac{[\text{MeOH}^+][\text{H}^+]}{[\text{Me}^{++}]}$$

$$K_{2\text{hyd.}} = \frac{[\text{Me}(\text{OH})_2][\text{H}^+]^2}{[\text{Me}^{++}]}$$

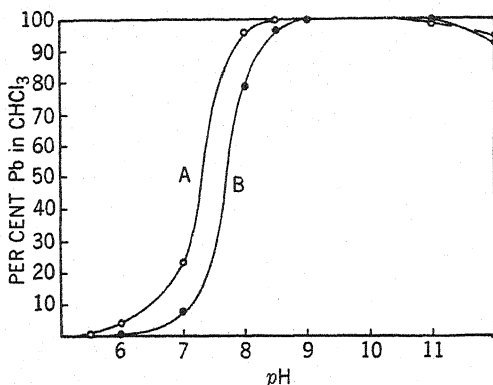


Fig. 15.—Extraction of lead with dithizone. Curve A: with 50% excess dithizone, Curve B: with 25% excess dithizone. (From data of Clifford and Wichmann, *J. Assoc. Official Agr. Chem.*, **19**, 134 (1936).)

This equation has not been tested experimentally. If the metal hydroxide has amphoteric properties and reacts with hydroxyl ions to form metalate ions another expression must be derived.

The values of the equilibrium constants of the various metal dithizonates have not yet been determined.<sup>8</sup> If they were known, it should be possible to state the fraction of metal in a solution of given pH that would be extracted with a specified volume of dithizone solution of known concentration (see, for example, p. 215). Moreover, it could then be predicted how

<sup>8</sup> A rough preliminary determination of the constant for cupric keto dithizonate in carbon tetrachloride has given the value  $10^{10}$ . The value was determined in 1 *M* hydrochloric acid and  $[\text{H}^+]$  in the equation was set equal to 1. For silver dithizonate a value of the order  $10^7$  has been obtained for  $K = \frac{[\text{AgDz}'\text{CCl}_4]}{[\text{Ag}^+]_w} \times \frac{[\text{H}^+]}{[\text{Dz}]\text{CCl}_4}$  from a determination in 6 *N* sulfuric acid.

successfully a given metal could be separated from one or more others in the same solution under specified conditions. At the present time our knowledge of the extractability of various metals is chiefly qualitative. Palladium, gold, mercury, silver and copper can be extracted in fairly acid solutions. These metals react in the order given, *i.e.*, palladium can be extracted from a more acid solution than can copper, or if palladium and copper are both present in a solution of low acidity, more palladium than copper will react with a restricted amount of dithizone. Bismuth can be extracted in weakly acid medium, while zinc, lead and other metals require a neutral or slightly alkaline solution for easy extraction. A number of

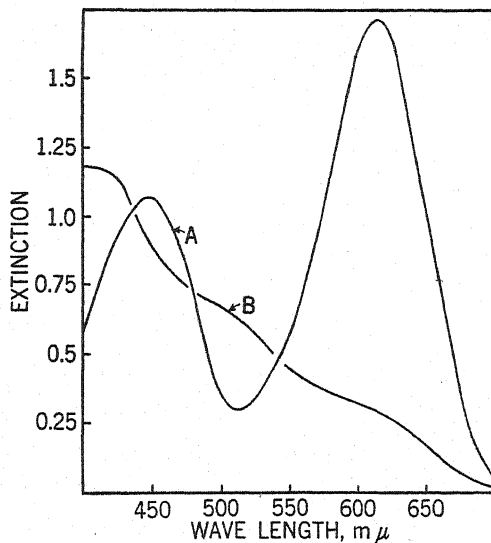


Fig. 16.—Absorption curves of (A) dithizone, and (B) its oxidation product, both in carbon tetrachloride solution. (According to Fischer and Weyl, *Wiss. Veröffentlich. Siemens-Konzern*, 14, No. 2, 41 (1935).)

metals such as lead, zinc and bismuth are less easily extracted as the  $pH$  is increased in the alkaline range. The behavior of lead is illustrated in Fig. 15 which is based on figures given by Clifford and Wichmann.<sup>9</sup> Some dithizonates are stable at high alkalinities (1  $N$  or stronger sodium hydroxide). Among these may be mentioned the complexes of cadmium, cobalt, nickel, copper, mercury and silver, some of which exist as the enol tautomer under the conditions.

<sup>9</sup> P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, 19, 130 (1936). See also p. 279 of this book.

### 3. Specificity of Dithizone Reactions

Although dithizone reacts with nearly a score of metals, the reaction can be made almost or quite specific for certain metals by resorting to one or more of the following devices:

1. Adjusting the  $pH$  of the solution to be extracted.
2. Altering the valence of interfering metals (of minor importance).
3. Adding a complex-forming agent which will tie up other reacting metals.

Separation of metals by the adjustment of the  $pH$  of the sample solution can be successfully carried out only with certain combinations of metals, namely those whose dithizonates have equilibrium constants differing markedly from each other. Extraction in a fairly acid (0.1 — 0.5  $N$ ) solution serves to separate such metals as palladium, silver, mercury and copper from other metals.<sup>10</sup> Lead and bismuth can be separated at  $pH$  3.0 (p. 280). By making a solution strongly basic (1  $N$  in sodium hydroxide) after adding citrate or tartrate to prevent precipitation of metal hydroxides, cadmium can be quantitatively extracted with a carbon tetrachloride solution of dithizone and separated from metals such as lead and zinc, but not from the noble metals, mercury, copper, cobalt and nickel.

Instead of extracting a metal from a solution of adjusted  $pH$  it is sometimes preferable with a low total content of reacting metals to extract under such conditions (for example, from a faintly ammoniacal solution) that other metals also are extracted, and then to shake the separated organic solvent containing the dithizonates with dilute acid of such concentration that the desired metal either remains in the organic solvent alone, or goes into the aqueous phase while the other dithizonates remain undecomposed. Thus if a carbon tetrachloride solution containing the dithizonates of copper, zinc and lead is shaken with one or two portions of dilute acid (0.05  $N$  or even weaker), copper remains in the carbon tetrachloride, while zinc and lead go into the aqueous phase.

Since this procedure is frequently applied, it may be worthwhile to consider how sharply separations of metals can be made in this way. By way

<sup>10</sup> A metal such as zinc which in small quantities does not react perceptibly with dithizone in a fairly acid solution will react if present in high concentration according to the law of mass action expressed by equation 1, p. 75, so that difficulties may arise when, for example, a trace of copper is to be determined in zinc metal. In such a case a perceptible amount of zinc may be extracted with the copper. If the amount of co-extracted zinc is not too great, the carbon tetrachloride or chloroform phase containing the two dithizonates may be drawn off and shaken with dilute acid which will decompose the zinc complex, thus leaving the copper dithizonate alone in the organic solvent (see p. 81). Another difficulty in a case of this kind may be the practical impossibility of the initial extraction of the trace metal on account of the reaction of most of the dithizone with the other metal present in much higher concentration.

of illustration, we may take two divalent metals whose dithizonates have the equilibrium constants  $10^{10}$  (metal L) and 100 (metal M).<sup>11</sup> Suppose that the metals are extracted with a  $4 \times 10^{-4} M$  (approximately 0.01 per cent weight by volume) solution of dithizone in an organic solvent, and the resulting solution of dithizonates is shaken with an equal volume of 0.01 *N* hydrochloric acid. First let us find the extent of decomposition of a pure  $2 \times 10^{-4} M$  solution of  $LDz'_2$ , containing no excess dithizone, under these conditions. It will be assumed that the equilibrium may be expressed by

$$\frac{[LDz'_2]_o}{[L^{++}]_w} = \frac{K[Dz]_o^2}{[H^+]_w^2},$$

*o* and *w* referring to the organic solvent and aqueous phases respectively. Since the volume of *o* is equal to the volume of *w*,

$$[Dz]_o = 2[L^{++}]_w$$

and

$$\begin{aligned} \frac{[LDz'_2]_o}{[L^{++}]_w} &= \frac{K \times 4[L^{++}]_w^2}{[H^+]_w^2} \\ [L^{++}]_w &= \sqrt[3]{\frac{[LDz'_2]_o[H^+]_w^2}{4K}}. \end{aligned}$$

Since the value of *K* is very large, the concentration of  $LDz'_2$  in the organic phase will change little on shaking with dilute acid, and it may be set equal to  $2 \times 10^{-4} M$ ; the concentration of metal in the aqueous phase when equilibrium is established is given by

$$[L^{++}]_w = \sqrt[3]{\frac{2 \times 10^{-4} \times 10^{-4}}{4 \times 10^{10}}} = 7.9 \times 10^{-7}.$$

(Any change in  $[H^+]$  is neglected.) The percentage of L going into the aqueous phase is therefore about 0.4. In any actual case, more or less free dithizone would be present and the amount of  $L^{++}$  going into the acid solution would be enormously reduced. Thus if the dithizone concentration of the organic solvent phase were  $4 \times 10^{-5} M$ ,  $\frac{[LDz'_2]_o}{[L^{++}]_w} = 1.6 \times 10^5$ . It is evident that the organic phase could be shaken successively with many fresh portions of 0.01 *N* acid without the loss of any significant amount of  $L^{++}$ , provided a little free dithizone is present.

To find the extent of decomposition of  $MDz'_2$  on shaking with acid, we

<sup>11</sup> The equilibrium constant of  $CuDz'_2$  in carbon tetrachloride is of the order  $10^{10}$  as already mentioned. The constant for  $ZnDz'_2$  in chloroform is approximately 3; the value in carbon tetrachloride is not known.

may first assume that all of  $M$  goes into the aqueous phase, and we then find

$$\frac{[MDz_2']_o}{[M^{++}]_w} = \frac{10^2 \times (4 \times 10^{-4})^2}{10^{-4}} = 0.16.$$

This value indicates that an appreciable amount of  $MDz_2'$  remains in the organic solvent and that the method of successive approximations should be applied in the calculation to obtain a more exact value. The exact value of  $[M^{++}]_w$  is found to be  $1.78 \times 10^{-4} M$ , which corresponds to 89 per cent decomposition of the dithizonate by acid. Evidently the organic solvent must be shaken with a fresh portion of 0.01  $N$  acid in order to decompose most of  $MDz_2'$ . If again an equal volume of acid is used,  $\frac{[MDz_2']_o}{[M^{++}]_w} = \text{ca. } 0.16$ , and  $[M^{++}]_w = 0.19 \times 10^{-4}$ . Accordingly two shakings with acid transfers  $(1.78 + 0.19) 100/2$  or 98.5 per cent of  $M$  to the aqueous phase. In other words,  $L$  and  $M$  can be separated in this way without much difficulty. As a matter of fact,  $M$  can be separated from a metal whose dithizonate has an equilibrium constant of  $10^5$  provided the free dithizone concentration during the shaking with acid is fairly high. Thus if  $[Dz] = 4 \times 10^{-4}$ , less than 1 per cent of the metal whose dithizonate constant is  $10^5$  would be brought into the aqueous phase when shaken with an equal volume of 0.01  $N$  acid, since the ratio of metal in organic solvent and acid will be  $\frac{10^5 \times (4 \times 10^{-4})^2}{10^{-4}} = 160$ . It appears then that

divalent metals whose dithizonate constants differ by the factor 1000 can be separated fairly satisfactorily in the way described by the proper choice of acid and free dithizone concentration, but a bigger difference in constants is desirable. The rate of attainment of equilibrium on shaking with acid is rapid, only 1 or 2 minutes of vigorous shaking generally being required.

As we have already seen, iron, tin and platinum do not form complexes with dithizone when present as  $Fe^{III}$ ,  $Sn^{IV}$  and  $Pt^{IV}$ .

Reagents forming stable complexes with interfering metals play an important role in dithizone procedures. It will be seen from Table 10 that the number of metals reacting with dithizone is greatly reduced in the presence of such complex forming agents as cyanide, thiocyanate and thiosulfate. A striking example is provided by the determination of lead. The only metals reacting in slightly basic medium containing cyanide are lead, univalent thallium, divalent tin, and bismuth. Since stannic tin does not react and bismuth can be separated from lead by extraction with dithizone in slightly acid medium, the only other metal which will interfere in the lead determination is thallium; a special procedure has been worked out for the determination of lead in its presence (p. 291).



At a pH of approximately 5 in the presence of a sufficient quantity of thiosulfate the only metals reacting appreciably with dithizone in carbon tetrachloride solution are zinc, stannous tin and palladium.<sup>12</sup> Large amounts of nickel and cobalt will react slightly under these conditions, but can be made harmless by the addition of cyanide, which also prevents the reaction of palladium. Sodium diethyldithiocarbamate has also been used as a general complex former in the determination of zinc after removal of copper (p. 451).

Some of the complex forming agents used in dithizone procedures are listed in Table 10. Further information will be found in the chapters dealing with the individual metals.

TABLE 10  
COMPLEX FORMING AGENTS IN DITHIZONE REACTIONS

Conditions	Metals reacting
Basic solution containing cyanide.....	Pb, Sn <sup>II</sup> , Tl <sup>I</sup> , Bi
Slightly acid solution containing cyanide.....	Pd, Hg, Ag, Cu
Dilute acid solution containing thiocyanate.....	Hg, Au, Cu
Dilute acid solution containing thiocyanate + cyanide...	Hg, Cu
Dilute acid solution containing bromide or iodide.....	Pd, Au, Cu
Slightly acid solution (pH 5) containing thiosulfate (CCl <sub>4</sub> solution of dithizone).....	Pd, Sn <sup>II</sup> , Zn (Cd)
Slightly acid solution (pH 4-5) containing thiosulfate + cyanide.....	Sn <sup>II</sup> , Zn
Citrate and tartrate in basic medium.....	Usually do not interfere with extraction of reacting metals (cf. p. 279 and p. 449).

#### 4. Colorimetric Determination of Metals by Dithizone

Dithizone determinations can be carried out by mono- or dicolor (mixed color) methods. In the mono color method, the aqueous solution after adjustment to the proper pH is shaken with successive portions of a carbon tetrachloride or chloroform solution of dithizone until it can be seen from the unchanged green color of the last portion that all of the metal has been extracted. The combined extracts are then shaken with a very dilute solution of a base, such as ammonium hydroxide, to remove excess dithizone. This step involves a source of error: if the alkalinity of the wash solution is too high some of the metal dithizonate may be decomposed, or if the alkalinity is not high enough, an appreciable amount of free dithizone may be left in the organic solvent. It is easier to remove dithizone from a carbon tetrachloride solution than from a chloroform

<sup>12</sup> H. Fischer and G. Leopoldi, *Z. anal. Chem.*, 107, 241 (1937).

solution. For 1:200 ammonium hydroxide, Clifford and Wichmann<sup>13</sup> found the partition coefficients to have the following values:

$$\frac{[Dz]_{NH_4OH}}{[Dz]_{CCl_4}} = 41 \text{ (31°C)} \quad \text{and} \quad \frac{[Dz]_{NH_4OH}}{[Dz]_{CHCl_3}} = 1.6 \text{ (30°C)}.$$

At pH 10 the respective coefficients are 19.4 and 0.76. Dithizone can be extracted from a carbon tetrachloride solution, but hardly at all from a chloroform solution, by an aqueous solution of pH 8. Offsetting the ease of removal of dithizone from carbon tetrachloride is the greater ease of decomposition of dithizonates in carbon tetrachloride than in chloroform when the organic solvent is shaken with an aqueous basic solution. The magnitude of the error when carbon tetrachloride is the solvent is illustrated by some figures given by Clifford and Wichmann. Twenty-five ml. of carbon tetrachloride containing lead dithizonate equivalent to 35.8  $\gamma$  of lead lost 6.4  $\gamma$  when shaken for 1 minute with 25 ml. of 1:200 ammonia; and when shaken for 10 minutes it lost 10.8  $\gamma$  (partial precipitation of lead in the aqueous phase). Another objection to the mono-color technique is the possibility of transformation of the keto complexes of certain metals into the enol tautomers on washing with an alkaline aqueous solution. Thus it is hardly possible to wash all the dithizone out of a carbon tetrachloride solution of keto copper dithizonate without forming some of the enol compound, as is made evident by a slight change in the hue of the originally violet solution (the enol dithizonate is brown). Mono color methods in which all of the excess dithizone must be removed from the organic solvent phase are not sound in principle. It is true that with some metals good results can be obtained, especially if the comparison solution is prepared under identical conditions, but the mixed color method is much to be preferred. If a photometer is available, the mono color method need rarely be used.

In the so-called mixed color method, the excess dithizone is allowed to remain in the organic solvent with the dithizonate. In visual work the hue of the solution is compared with a series of standards, all prepared with the same amount of dithizone as the sample solution. The standards exhibit a series of hues ranging from the unchanged green of the dithizone to the color of the metal dithizonate alone. The comparison is conveniently made in glass-stoppered tubes (p. 42), and the organic solvent layers are examined transversely against a white background. The dithizone solution should not be stronger than 0.001 per cent *w/v*, else the solutions will be too strongly colored for comparison at a depth of 1–2 cm. If the approximate amount of the metal is not known, the dithizone solution is added in small portions from a buret with shaking after each

<sup>13</sup> P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **19**, 130 (1936).

addition until a suitable mixed color is obtained.<sup>14</sup> A carbon tetrachloride or chloroform solution containing somewhere near equal amounts of dithizone and dithizonate gives the most satisfactory hue for precise comparison.<sup>15</sup> A grayish mixed color is then obtained with red or violet-red dithizonates, and the eye can detect differences of about 3 per cent in the metal concentration.

When a spectrophotometer is used in determining a metal by the mixed color method there are usually two possibilities in the choice of a wave length. One may measure the absorption of light by the metal complex or by the excess of dithizone remaining after the reaction is completed. In carbon tetrachloride, the approximate wave lengths ( $m\mu$ ) of maximum absorption by dithizone and the keto dithizonates of some of the common

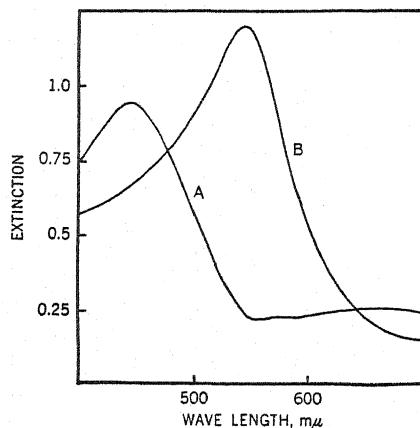


Fig. 17.—Absorption curves of (A) enol, and (B) keto cupric dithizonate in carbon tetrachloride (Fischer and Weyl).

metals (Figs. 16, 17, 18, 19) are the following according to H. Fischer and others:

Dithizone	620, 450 (secondary)
Bismuth	500
Cadmium	520
Copper (II)	510
Lead	525
Mercury (II)	530
Silver	460
Zinc	535

<sup>14</sup> If the reaction between metal and dithizone proceeds sufficiently rapidly the colorimetric titration technique can be applied, *i.e.*, a standard solution of the metal is added to a solution of the same pH as the unknown and containing the same volume of dithizone, until after thorough shaking the hues of the organic solvents match.

<sup>15</sup> H. Grubitsch and J. Sinigoj, *Z. anal. Chem.*, **114**, 30 (1938).

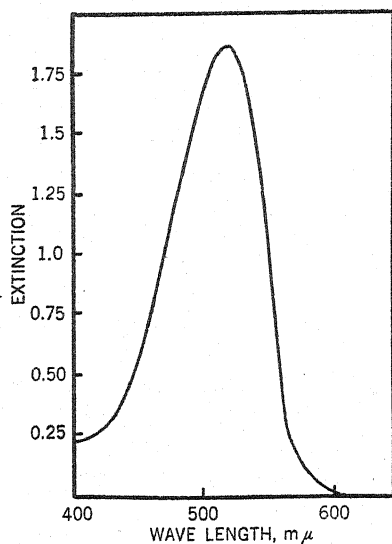


Fig. 18.—Absorption curve of lead dithizonate in carbon tetrachloride (Fischer and Weyl).

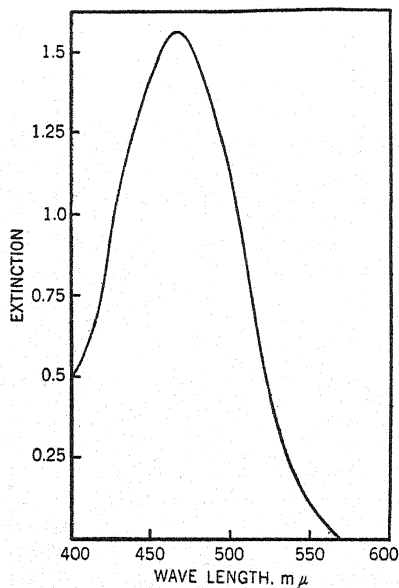


Fig. 19.—Absorption curve of silver keto dithizonate in carbon tetrachloride (Fischer and Weyl).

It will be seen from Fig. 16 that there is a minimum in the absorption curve of dithizone at about 510  $m\mu$ , or close to the wave length of maximum

absorption of the dithizonates of most of the metals listed above. On the other hand most of these dithizonates in carbon tetrachloride solution absorb very little light above  $600\text{ m}\mu$ , whereas the strongest absorption is shown by dithizone at approximately  $620\text{ m}\mu$ . Therefore by using light of a wave length in the neighborhood of  $620\text{ m}\mu$ , or a suitable red filter, high sensitivity can be obtained in mixed color methods. When the reaction must be carried out in a basic medium at a  $p\text{H}$  at which some of the dithizone goes into the aqueous phase, it is usually better to measure the absorption of the metal complex instead of that of the residual dithizone.

Since both dithizone and the dithizonates of copper, zinc, lead, etc. obey Beer's law in carbon tetrachloride or chloroform, a plot of the extinction of a dithizone-dithizonate solution against the metal concentration in the organic solvent gives a straight line, provided the light is "monochromatic." When a filter is used, deviation from linearity may occur (see, for example, Fig. 44, p. 322). If a sufficient excess of dithizone is present in the mixture, the extinction will be proportional to the amount of the metal originally present in the aqueous phase. When the excess of dithizone becomes very small, dissociation of the dithizonate may be sufficiently great to cause failure of this relation.

A metal frequently can not be determined directly with dithizone in the solution of the sample: oxidizing agents attacking dithizone to a greater or less extent may be present, it may be difficult to adjust the acidity of the solution to the exact value required, and there may be interference from other heavy metals or even neutral salts. When such conditions exist, a preliminary extraction with dithizone (0.01 per cent  $w/v$ ) is made to separate completely the metal in question. The dithizonate in the organic solvent layer may next be decomposed and the metal converted into ionic form for final determination in a number of ways:

1. The dithizonates of lead, zinc, cadmium, and thallium are readily decomposed and the metal transferred to the aqueous phase when the organic solvent is shaken with dilute acid.<sup>16</sup> As we have already seen, this procedure provides a separation from such metals as copper whose dithizonates are not appreciably attacked by dilute acids.
2. The organic solvent phase may be evaporated to dryness and the dithizonate residue may be heated with a few drops of concentrated sulfuric acid and perchloric acid to destroy organic matter completely. This method may be used for copper and other metals forming dithizonates not decomposed by dilute acids.
3. The organic solvent may be shaken with an acid solution of a strong oxidizing agent such as potassium permanganate, ceric sulfate, or

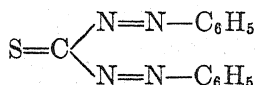
<sup>16</sup> Zinc and cadmium dithizonates in carbon tetrachloride or chloroform may be decomposed with 0.01-0.02  $N$  hydrochloric acid (p. 450). Lead dithizonate is decomposed at even lower acidities.

bromine to destroy the dithizonate radical or any free dithizone (conversion to the diazone and also other oxidation products. The metal enters the aqueous phase and the excess of the oxidizing agent can be destroyed by a suitable reducing agent such as hydroxylamine hydrochloride.<sup>17</sup> This procedure has been used to decompose mercuric dithizonate, which can not be treated by either of the two preceding methods.

4. The organic solvent solution of the dithizonate may be shaken with an aqueous solution of a reagent forming a stable complex with the metal. This method has been applied in decomposing silver and mercuric dithizonates. Before the metal in the aqueous layer can be determined with dithizone, the complex must be destroyed or at least made much weaker compared to the dithizone complex by a change in conditions, *e.g.*, in the acidity (see p. 320 for an example).

#### 5. Oxidation of Dithizone

Dithizone is oxidized to diphenylthiocarbodiazone



under weak oxidizing conditions.<sup>18</sup> This compound is insoluble in acid and basic aqueous solutions, but it dissolves in chloroform and carbon tetrachloride to give a yellow or brown solution. It does not react with metals. This oxidation product is sometimes present in commercial dithizone and the purification of the reagent is based on the insolubility of the thiocarbodiazone in ammonia (see below).

Ferric iron oxidizes dithizone, especially in basic solution (containing citrate or tartrate). The oxidation by iron is very pronounced in alkaline cyanide solutions. Copper in basic cyanide solutions also oxidizes the reagent. Low concentrations of the halogens, nitrous acid, permanganate, etc. produce the yellow or brown oxidation product at least in part. Under strong oxidizing conditions dithizone is decomposed, the sulfur of the compound being attacked and a splitting of the molecule occurring. If dithizone has been oxidized only as far as to diphenylthiocarbodiazone, regeneration of the dithizone can be effected by the action of reducing agents such as hydroxylamine hydrochloride and sulfur dioxide.

<sup>17</sup> When bromine is used as oxidizer, the aqueous solution may be evaporated to dryness and residue heated with a mixture of concentrated sulfuric, nitric and perchloric acids to destroy any organic matter. See C. A. Greenleaf, *J. Assoc. Official Agr. Chem.*, **24**, 337 (1941).

<sup>18</sup> H. Fischer, *Angew. Chem.*, **50**, 919 (1937); E. Fischer, *Ann.*, **212**, 316 (1882).

Oxidation of dithizone by ferric iron and other oxidizing agents naturally leads to difficulties in quantitative work and even in qualitative (confusion of the yellow color produced with that given by mercury and silver dithizonates). The oxidation can in large measure be prevented by adding hydroxylamine hydrochloride to the aqueous solution to be extracted. A preliminary extraction of the metal will often be necessary in practical work in order that difficulties due to oxidizing agents may be avoided.

#### 6. *Purification of Dithizone. Stability of Dithizone Solutions*

Purification of dithizone is not always necessary. Some of the products sold are fairly pure. If a 0.01 per cent solution in carbon tetrachloride yields a carbon tetrachloride layer that is colored only a faint yellow after shaking with dilute (1:100) metal-free ammonia, the product may ordinarily be used as it is. The presence of a small amount of the yellow oxidation product in dithizone is usually of no importance. Only when minute traces of such metals as lead and cadmium are determined by extraction from a fairly basic solution is the yellow color of the carbodiazone likely to prove disturbing. When purification is deemed desirable one may proceed as follows. One-half gram of dithizone is dissolved in 50 ml. of chloroform and the solution is filtered through a coarse fritted glass crucible to remove any insoluble material. The solution is shaken in a separatory funnel with 4 successive portions of pure 1:100 ammonia, each 50 to 75 ml. in volume. The aqueous extracts are separated from the chloroform and filtered through a small plug of cotton to remove droplets of chloroform. The ammoniacal solution is made slightly acid with pure hydrochloric acid to precipitate dithizone, which is extracted with 2 or 3 portions of chloroform each having a volume of 15-20 ml., and the combined chloroform extracts are shaken twice with an equal volume of pure water. The chloroform solution is delivered into a beaker and the chloroform evaporated off at 50° C. The product may be dried in a desiccator.

Both chloroform and carbon tetrachloride solutions of dithizone decompose rapidly with formation of the carbodiazone if exposed to strong light and subjected to relatively high temperatures. High temperatures, such as exist in many laboratories during the summer months, have a greater effect than diffuse light. Direct sunlight bleaches dithizone solutions rapidly. Clifford<sup>19</sup> states that sunlight acts on the solvent (chloroform), rather than on the reagent directly, to yield decomposition products such as phosgene which then oxidize the dithizone.

In order to prepare a stable dithizone solution it is necessary to use chloroform and carbon tetrachloride free from oxidizing substances. Clifford<sup>19</sup> recommends the procedure of Biddle<sup>20</sup> for the purification of

<sup>19</sup> P. A. Clifford, *J. Assoc. Official Agr. Chem.*, **21**, 695 (1938).

<sup>20</sup> D. A. Biddle, *Ind. Eng. Chem., Anal. Ed.*, **8**, 99 (1936).

chloroform. This procedure may be used both for the recovery of chloroform from used dithizone solutions, and for improving the quality of U. S. P. chloroform. It is carried out as follows. The chloroform, separated from any aqueous phase, is washed until colorless with commercial sulfuric acid equal to 5 or 10 per cent of its volume, and is then treated with lime to remove sulfuric acid. The chloroform is distilled in the presence of a little lime, and alcohol is added to the distillate to the extent of 1.0–1.5 per cent of its volume. The alcohol acts as a preservative, and Clifford has shown that it is more effective as such if it is freshly distilled from potassium hydroxide, instead of being added as the ordinary 95 per cent material. It is advisable to add the calculated amount of alcohol to the receiver before the distillation is begun, and to swirl the contents of the receiver during distillation so as to mix the alcohol and chloroform. The distillation should be carried out in an all-glass apparatus, and heating should be done with a water bath.

Dithizone solutions prepared from chloroform thus purified are quite stable if stored at 40° F. in the dark. A chloroform solution containing 4 mg. of dithizone per liter lost 5 per cent in strength after 6½ months storage under these conditions (Clifford). Overlaying a chloroform-dithizone solution with an aqueous solution of sulfur dioxide or hydroxylamine hydrochloride does not increase the stability of the solution.

Carbon tetrachloride is purified in the same manner as chloroform except that alcohol is not added as a preservative. Contrary to the behavior of chloroform solutions, carbon tetrachloride dithizone solutions are stabilized by covering with a 0.1 *M* solution of sulfur dioxide<sup>21</sup> in water having about one-tenth the volume of the organic solvent. A carbon tetrachloride solution of dithizone so protected showed no appreciable change in strength after being kept for 9 months at 40° F. in the dark (Clifford). Two weeks should be allowed to elapse after preparation of the solution and before it is used. It may then be considered to have reached a constant strength (reduction of any diphenylthiocarbodiazone present). Carbon tetrachloride solutions protected by sulfurous acid may be used for the determination of lead and zinc but naturally not for metals that are easily reduced.

It may not always be worth while to go to all the trouble mentioned above in purifying carbon tetrachloride and chloroform and preparing the solutions. In much work with dithizone it suffices to make up a 0.01 per cent stock solution in *analytical reagent* carbon tetrachloride. This solution will

<sup>21</sup> H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **119**, 168 (1940), found a weakly acid solution of hydroxylamine hydrochloride to be slightly better than sulfurous acid for stabilizing a carbon tetrachloride solution of dithizone (*cf.* p. 291), whereas Clifford found the reverse to be true.



show but little change for weeks if kept cool and in the dark. It may be used to prepare the 0.001 per cent *w/v* dithizone solution commonly used in the final determinations. The more dilute solution may be made up in sufficient quantity to last for a few days. It will usually show a progressive loss in strength, but this is immaterial if its strength is checked at the time the photometric determinations are made. The time required to check one or two points on the standard curve may be less than that required to redistil the organic solvents, etc. to obtain a more stable solution which also will have to be checked at intervals for assurance.

The purity of the organic solvent is of greater importance when dithizone is used in an acid solution than when it is used in slightly basic medium. It has been found that some carbon tetrachloride (not reagent quality) contains a substance, probably a sulfur compound, which markedly inhibits the reaction of dithizone with copper in 0.1 *N* mineral acid solution. Only analytical-grade carbon tetrachloride should be used for making up dithizone solutions to be employed in the determination of copper and other metals in acid medium. Shaking impure carbon tetrachloride with a dilute aqueous copper solution or a calcium hydroxide solution, followed by distillation, may be expected to be effective in removing the impurity, but no tests on this point have been made.

#### *7. Errors in Dithizone Methods*

The following are some important possible sources of error in the determination of metals by dithizone which the trace analyst must always bear in mind:

1. Interference from other reacting metals.
2. Incomplete extraction of the dithizonate in a preliminary separation.
3. a. Decomposition of the dithizonate in an organic solvent on washing with an alkaline solution.  
b. Incomplete removal of free dithizone from the organic solvent in a mono-color method.
4. Separation of solid dithizonate because of low solubility in the organic solvent (may occur with carbon tetrachloride).
5. Oxidation of dithizone.
6. Adsorption (or coprecipitation) by precipitates in the solution to be extracted.
7. Instability of standard dithizone solutions and also of dithizonates.
8. Heavy metals in reagents and distilled water.

Some of these errors (3*a* and *b*) have already been considered in the previous discussion, and it has been shown that interference from other metals can be prevented in many cases by the proper adjustment of the acidity and the use of complex forming agents. Such measures do not

always succeed however if large quantities of foreign metals are present and the analyst must always be on his guard against the possible interference of other metals. This source of error is considered further under the respective metals.

Error (2) is easily avoided by extracting the solution at the proper acidity with an excess of dithizone and shaking for a sufficient length of time; by using a sufficient number of portions of dithizone in the extraction, the quantity of metal in the aqueous phase can usually be reduced to insignificant proportions. It has been noticed that certain metals hinder the extraction of dithizonates. Thus it has been found that relatively small amounts of titanium (5 mg. and more in a volume not specified) prevent the complete extraction of lead from an ammoniacal citrate medium (pH varied from 7 to 11).<sup>22</sup> A comparatively high concentration of aluminum under the same conditions makes the extraction of lead difficult, and a larger number of portions of dithizone is then required for quantitative extraction. Preliminary isolation of lead as sulfide is to be recommended in these cases. H. Fischer noted that aluminum prevented the complete extraction of zinc in a faintly acid solution. The effect of titanium and aluminum may possibly be due to a hydrolysis which results in the formation of a colloidal dispersion having strong adsorptive properties (point 6 above).

The solubility of dithizonates in carbon tetrachloride is not great, and if the metal or dithizone concentration is high the dithizonate may be precipitated. It then forms flocs in the organic solvent or gathers as a scum at the interface of the two liquids, and losses can then occur in the separation of the carbon tetrachloride and in washing. This error can be avoided by working with smaller amounts of metal. In general the accuracy of a dithizone procedure is not increased by working with large amounts of metal. For example, results with 10  $\gamma$  of a metal are as accurate as with 100  $\gamma$ , and can as a matter of fact be obtained more conveniently and more rapidly because of the smaller volumes involved. If for any reason it should be necessary to extract a large amount of a metal ( $> 100 \gamma$ ), a chloroform dithizone solution is preferable to a carbon tetrachloride solution because of the greater solubility of dithizonates in the former. The comparative advantages of carbon tetrachloride and chloroform solutions on other grounds were considered in the last section. Unless chloroform has special advantages, carbon tetrachloride is preferred as a solvent because of its lesser volatility, greater density and lower solubility in water.

The formation of a precipitate or a turbidity in an aqueous solution to be extracted with dithizone must be regarded with suspicion. Thus solutions of samples high in phosphorus (biological material) may give a precipitate

<sup>22</sup> J. Schultz and M. A. Goldberg, *Ind. Eng. Chem., Anal. Ed.*, **15**, 155 (1943).

of calcium phosphate on addition of ammonia, even if citrate is present, and such a precipitate will carry down the greater part of the lead in the solution. Metastannic acid will also retain lead.

Since dithizone solutions are not very stable, standard curves for use in photometry with a particular solution should be checked at frequent intervals. Dithizonate solutions should not be allowed to stand for any length of time before their transmittancy is determined and they should be protected from strong light.<sup>23</sup> Dithizonates extracted from basic medium are sometimes quite unstable (cadmium dithizonate from strong sodium hydroxide solution is an example) and the color fades fairly rapidly. In the standard series method it is preferable to prepare the standards at the same time that the sample is treated.

Reagents for use in dithizone methods should be purified by appropriate methods (p. 14). Redistilled water and ammonia must be used. Redistilled acids are desirable but not necessary. Weakly basic and neutral solutions can frequently be freed from reacting heavy metals by extracting them with dithizone. The glassware employed should be of Pyrex (see p. 13). Vessels should be rinsed with dilute acid before use. Blanks must always be run.

## II. Di- $\beta$ -Naphthylthiocarbazone<sup>24</sup>

The dinaphthylthiocarbazone exhibits the same general properties as the diphenylthiocarbazone. Suprunovich<sup>24</sup> states that the sensitivity of the reactions of the former with heavy metals is greater than that of dithizone, but Hubbard<sup>24</sup> found no significant difference between the two reagents in the determination of lead and bismuth. The colors of the corresponding lead and bismuth compounds are fairly different, and the colors of the mercury (II) salt markedly so, as shown by Hubbard:

Metal	Color with Dinaphthylthiocarbazone (CHCl <sub>3</sub> )	Color with Dithizone (CHCl <sub>3</sub> )
Hg	Red (blue shade)	Yellow-orange
Pb	Purple	Rose-red
Bi	Magenta	Orange

<sup>23</sup> Mercuric dithizonate (keto) shows a peculiar behavior when exposed to strong light. The yellow-orange color of the organic solvent changes to green; the color change is reversed when the solution is placed in darkness or in subdued light. The light sources in some photometers are sufficiently intense to cause a fairly rapid change in the transmittancy of the solution, and readings must be made without delay.

<sup>24</sup> For the preparation of this compound see I. B. Suprunovich, *J. Gen. Chem. U. S. S. R.*, **8**, 839 (1938); M. Preund, *Ber.*, **24**, 4178 (1891); D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, **12**, 768 (1940). D. M. Hubbard and E. W. Scott, *J. Am. Chem. Soc.*, **65**, 2390 (1943).

The minimum transmission of solutions of the naphthylthiocarbazone complexes lies at higher wave lengths than the minimum of the solutions of the corresponding dithizone complexes.

Because of the red color of mercuric dinaphthylthiocarbazonate, the use of dinaphthylthiocarbazone is preferable to that of dithizone in the determination of mercury by the mixed color technique, and a method for this metal involving the use of the new reagent has been described by Hubbard.<sup>24</sup>

### III. Diphenylcarbazine and Diphenylcarbazone



These compounds react with heavy metals such as mercury (I and II), copper, cadmium, etc. in weakly acid solution to yield internal complex salts having blue, violet or reddish colors.<sup>25</sup> The products can be extracted with chloroform and other solvents. It appears that the reaction of diphenylcarbazine first involves its air-oxidation to diphenylcarbazone which is the active reagent in the reaction with the metals mentioned, but the exact course of the reaction is obscure. These reagents are not very suitable for the determination of any heavy metal (except chromium as chromate), although the carbazone has been used to some extent in the past for the determination of mercury; it is far inferior to dithizone for the purpose. Derivatives of diphenylcarbazine and carbazone, and also the dinaphthyl compounds, have been prepared and used qualitatively.<sup>26</sup>

Diphenylcarbazine is an excellent reagent for the determination of chromium (VI), with which in dilute mineral acid solution it gives a soluble red-violet compound of unknown constitution.<sup>27</sup> Pure diphenylcarbazone does not react with chromium (VI). Molybdate also gives a red-violet color with diphenylcarbazine, but the reaction is much less sensitive than the one with chromate. Vanadate, permanganate, and ferric iron give brown colors with diphenylcarbazine and thus interfere in the determination of chromium. The chromium-diphenylcarbazine compound is not extractable with the usual organic solvents.

An indirect colorimetric method for the determination of lead is based on its precipitation as chromate or as the double chromate  $\text{K}_2\text{Pb}(\text{CrO}_4)_2$  and the determination of chromate with diphenylcarbazine in the acid solution of the washed precipitate.<sup>28</sup>

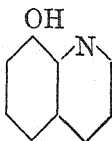
<sup>25</sup> F. Feigl and A. Lederer, *Monatsh.*, **45**, 63, 115 (1924).

<sup>26</sup> P. Krumholz and F. Hönel, *Mikrochim. Acta*, **2**, 177 (1937).

<sup>27</sup> P. Cazeneuve, *Compt. rend.*, **131**, 346 (1900). See further p. 191.

<sup>28</sup> T. V. Letonoff and J. G. Reinhold, *Ind. Eng. Chem., Anal. Ed.*, **12**, 280 (1940).

## IV. 8-Hydroxyquinoline (Oxine)



This reagent forms slightly soluble internal-complex salts with most metals. These complexes have the general formula  $\text{Me}^{+n}(\text{C}_9\text{H}_6\text{ON})_n$  (some exceptions are noted in Table 11). Determinations are usually made gravimetrically or volumetrically,<sup>29</sup> but colorimetric determination of metals is also possible. Most of the hydroxyquinolates are soluble in chloroform, yielding solutions of strong color (ferric iron and vanadium green-black, aluminum and other metals yellow) and some metals may thus be determined by direct colorimetry.<sup>30</sup> A number of metals, notably aluminum, gallium, indium, and zinc, give hydroxyquinolates which are strongly fluorescent in chloroform solution and can be determined fluorimetrically (p. 239).

The pH ranges of virtually complete extraction of some hydroxyquinolates by chloroform and the wave lengths of maximum absorption of the resulting solutions are as follows: ferric iron, 1.9 – 3.0 (470, 570 m $\mu$ ); aluminum, 4.3 – 4.6 (395 m $\mu$ ); bismuth, 4.0 – 5.2 (395 m $\mu$ ); cobalt, >6.8 (420 m $\mu$ ); nickel, >6.7 (395 m $\mu$ ); and cupric copper, 2.7 – >7.0 (410 m $\mu$ ).<sup>31</sup> For the determination of indium see p. 257. 8-Hydroxyquinoline alone in chloroform absorbs strongly below ca. 375 m $\mu$ . Beer's law is followed by the solutions of these metal complexes at low concentrations (up to 10 p.p.m.).

The indirect colorimetric determination of metals by oxine is more generally applicable than the direct determination, and can be carried out in a number of ways after the hydroxyquinolate precipitate has been collected by filtration and washed free of excess oxine:

1. The oxine in the precipitate can be coupled with a diazo compound to yield a dye of strong color. Thus, Alten, Weiland and Loofmann,<sup>32</sup> in the colorimetric determination of aluminum, dissolve the oxinate in a mixture of equal volumes of dilute hydrochloric acid and alcohol, add a mixture of

<sup>29</sup> See the monograph of R. Berg, *Die analytische Verwendung von o-Oxychinolin (Oxin) und seiner Derivate*. 2nd ed., Enke, Stuttgart, 1933 (Vol. XXXIV in the series *Die Chemische Analyse*).

<sup>30</sup> The feasibility of determining small quantities of aluminum in this manner was shown by G. H. Bendix in unpublished studies at the University of Minnesota in 1937.

<sup>31</sup> T. Moeller, *Ind. Eng. Chem., Anal. Ed.*, **15**, 346 (1943). In each case, 25 ml. of aqueous solution were extracted with four 5 ml. portions of 0.01 M 8-hydroxyquinoline solution in chloroform.

<sup>32</sup> F. Alten, H. Weiland and H. Loofmann, *Angew. Chem.*, **46**, 668 (1933).

sulfanilic acid and sodium nitrite in acetic acid, allow to stand for 10 minutes, and then make alkaline with sodium hydroxide. The yellow-red solution is compared with a standard similarly prepared.

TABLE 11  
SOME METAL HYDROXYQUINOLATES

Metal	pH Range for Complete Precipitation <sup>a</sup>	Solubility in Chloroform <sup>b</sup>
Aluminum.....	4.2-9.8	S
Antimony.....	>1.5	
Bismuth.....	4.8-10.5	S
Cadmium.....	5.4-14.6	S
Calcium.....	9.2-13	I
Cerium (III).....	Faintly basic	
Chromium (III).....	Slightly basic	
Cobalt.....	4.3-14.5	S
Copper.....	5.3-14.6	S
Gallium.....	ca. 6-8	S
Indium.....	Acetic acid-acetate	S
Iron (III).....	2.8-ca. 12	S
Lead.....	8.4-12.3	S
Magnesium.....	9.4-12.7	I
Manganese.....	5.9-10.0	S
Molybdenum <sup>c</sup> .....	3.6-7.3	S
Nickel.....	4.3-14.6	S
Palladium.....	Dilute HCl	S
Scandium.....		S
Thorium <sup>d</sup> .....	4.4-8.8	S
Titanium <sup>e</sup> .....	4.8-8.6	S
Tungsten <sup>f</sup> .....	5.0-5.7	I
Uranium <sup>g</sup> .....	5.7-9.8	S
Vanadium.....	Acetic acid-acetate	S
Zinc.....	4.6-13.4	S
Zirconium.....	Acetic acid-acetate	S

<sup>a</sup> Values for Co, Cu, Mg, Ni, W, U and Zn from H. R. Fleck and A. M. Ward, *Analyst*, 58, 3888 (1933); most of the others from H. Gotô, *J. Chem. Soc. Japan*, 54, 725 (1933); 56, 314 (1935).

<sup>b</sup> S = extracted, I = not extracted.

<sup>c</sup> Formula of hydroxyquinolate  $\text{MoO}_2(\text{C}_6\text{H}_5\text{ON})_2$

<sup>d</sup>  $\text{Th}(\text{C}_6\text{H}_5\text{ON})_4 \cdot \text{C}_6\text{H}_5\text{ON}$

<sup>e</sup>  $\text{TiO}(\text{C}_6\text{H}_5\text{ON})_2$

<sup>f</sup>  $\text{WO}_2(\text{C}_6\text{H}_5\text{ON})_2$

<sup>g</sup>  $\text{UO}_2(\text{C}_6\text{H}_5\text{ON})_2 \cdot \text{C}_6\text{H}_5\text{ON}$

2. Phosphotungstic, molybdotungstic, and phosphotungstomolybdic acid are reduced by oxine in basic medium and the resulting blue solution containing tungsten or molybdenum in a lower valence can be compared with a standard obtained in the same way.<sup>33</sup>

<sup>33</sup> M. Teitelbaum, *Z. anal. Chem.*, 82, 366 (1930). R. Berg, W. Wölker, and E. Skopp, *Mikrochemie (Emich Festschrift)*, 1930, p. 18.

3. Certain quinolate precipitates, *e.g.*, magnesium quinolate, may be dissolved in dilute acid and a ferric chloride solution added to give a green solution (maximum absorption at about 650 m $\mu$ );<sup>34</sup> or they may be converted into ferric quinolate which is filtered off and dissolved in alcohol (green-black color).<sup>35</sup>

By adjusting the pH of the solution, various separations can be made with oxine (*cf.* Table 11). Also by the addition of complex-forming agents certain separations become possible. For example, in sodium hydroxide-tartrate medium iron (III) is not precipitated whereas magnesium is precipitated. In acetic acid solution containing malonic acid, iron (III) is precipitated but not aluminum, etc. A consideration of the various separations possible lies outside the scope of this book, but these separations may be found useful in colorimetric as well as in gravimetric and volumetric oxine determinations and should be borne in mind.<sup>36</sup>

Oxine is generally dissolved in alcohol, acetone or acetic acid for use as a precipitant. Certain hydroxyquinolates such as those of iron (III) and aluminum are readily soluble in organic solvents and such metals should be precipitated with an acetic acid solution of the reagent. Oxine is but slightly soluble in water and errors may arise from the precipitation of the reagent itself in certain cases, and possibility of error from this source must be taken into consideration. The use of an unregulated excess of oxine in precipitations must be avoided.

### 8-Hydroxyquinoline-5-sulfonic Acid

This compound and its halogen derivatives (in the 7-position) have been used for the colorimetric determination of ferric iron and vanadium.<sup>37</sup>

### 8-Hydroxyquinoline and Iodide

Oxine and iodide form a complex iodide with bismuth in dilute acid solution which can be extracted by amyl acetate or a mixture of amyl acetate and acetone (orange colored solution).<sup>38</sup>

<sup>34</sup> R. Wolff, *Compt. rend. soc. biol.*, **127**, 1445 (1938). L. Gerber, R. I. Claassen and C. S. Boruff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 660 (1942). M. E. Weeks and J. R. Todd, *ibid.*, **15**, 297 (1943).

<sup>35</sup> J. Lavollay, *Bull. soc. chim. biol.*, **17**, 432 (1935).

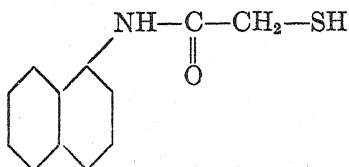
<sup>36</sup> For further information see W. Proding, *Organic Reagents Used in Quantitative Inorganic Analysis* (translated by S. Holmes). Elsevier, New York, 1940; pp. 103-112. G. E. F. Lundell and H. B. Knowles, *Bur. Standards J. Research*, **3**, 91 (1929).

<sup>37</sup> J. Molland, *Tids. Kjemi Bergvesen*, **19**, 119 (1939); *Arch. Math. Naturvidenskab.*, **43**, 67 (1940).

<sup>38</sup> R. Sazerac and J. Pouzergues, *Compt. rend. soc. biol.* **109**, 79, 370 (1932).

## 5,7-Dibrom-8-hydroxyquinoline

This reagent precipitates titanium, copper and iron (III) from mineral acid solution.<sup>39</sup>

V. Thioglycolic  $\beta$ -aminonaphthalide (Thionalide)

Thionalide yields very slightly soluble white or pale-colored salts of the type  $\text{Me}^{\text{II}}(\text{C}_{12}\text{H}_{10}\text{ONS})_2$  with most of the metals of the hydrogen sulfide

TABLE 12  
SENSITIVITY OF PRECIPITATION OF METALS BY THIONALIDE<sup>a</sup>  
(In 0.2 N mineral acid solution)

Metal	Limiting concentration
Cu	1:10 <sup>7</sup>
Ag	1:5 × 10 <sup>8</sup>
Au	1:2.5 × 10 <sup>8</sup>
Hg	1:1.5 × 10 <sup>7</sup>
Sn	1:1.25 × 10 <sup>7</sup>
As	1:10 <sup>8</sup>
Sb	1:4 × 10 <sup>7</sup>
Bi	1:10 <sup>7</sup>
Pt	1:10 <sup>7</sup>
Pd	1:10 <sup>7</sup>

<sup>a</sup> According to R. Berg.

group.<sup>40</sup> The reagent is used chiefly for the gravimetric or volumetric determination of these metals, but it also finds application in their indirect colorimetric determination, which is based on the reduction of phosphotungstomolybdic acid by the thionalide in the metal complex (see the determination of thallium, p. 412). The nephelometric determination of copper, mercury, and arsenic by thionalide has been described.<sup>41</sup>

Thionalide, like hydrogen sulfide, precipitates copper, silver, gold, mercury, tin, arsenic, antimony, bismuth, platinum, palladium, rhodium,<sup>42</sup> and ruthenium<sup>43</sup> from dilute mineral acid solutions. The precipitates are

<sup>39</sup> R. Berg and H. Küstenmacher, *Z. anorg. allgem. Chem.*, **204**, 215 (1932).

<sup>40</sup> R. Berg and O. Roebling, *Ber.*, **68**, 403 (1935); *Angew. Chem.*, **48**, 430, 597 (1935). R. Berg and E. S. Fahrenkamp, *Z. anal. Chem.*, **103**, 305 (1937); **112**, 162 (1938).

<sup>41</sup> R. Berg, E. S. Fahrenkamp, and W. Roebling, *Mikrochemie (Molisch Festschrift)*, 1936, p. 42.

<sup>42</sup> H. Kienitz and L. Rombock, *Z. anal. Chem.*, **117**, 241 (1939).

<sup>43</sup> W. J. Rogers, F. E. Beamish, and D. S. Russell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 561 (1940).

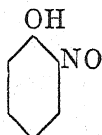


extremely slightly soluble (Table 12). Unlike hydrogen sulfide, thionalide does not precipitate lead and cadmium in dilute mineral acid medium. In a tartrate solution made basic with sodium carbonate, copper, gold, mercury, cadmium, and thallium are precipitated; in an alkaline cyanide-tartrate solution, gold, thallium, tin, lead, antimony, and bismuth are precipitated; in a sodium hydroxide-cyanide-tartrate solution only thallium is precipitated. Thionalide is superior to hydrogen sulfide as a precipitant because coprecipitation is less and the precipitates have the theoretical composition.

Thionalide is readily soluble in the common organic solvents, but only slightly soluble in water or dilute mineral acid medium. In water the solubility in 100 ml. is 0.01 g. at 20° and 0.08 g. at 95°. Acetic acid increases the solubility. Usually a 1 per cent solution of the reagent in ethyl alcohol or glacial acetic acid is used. The solution decomposes in a few hours and should be prepared fresh before use.

The solvent effect of alcohol or acetic acid on the metal-thionalide complexes is not of importance as long as the volume of the organic solvent is not greater than 10 to 15 per cent. Oxidizing agents, including ferric iron, destroy the reagent, and hydroxylamine sulfate should be added before precipitation when these are present.

## VI. Orthonitrosophenol



This reagent forms highly colored internal complexes with a number of heavy metals in faintly acid solution.<sup>44</sup> The reagent itself can be prepared only in solution.<sup>45</sup> It is generally used in the form of a petroleum ether solution, which is stable for 2-3 weeks if kept in a refrigerator. This solution has a yellowish green color.

With the following metals *o*-nitrosophenol gives salts soluble in water or in certain organic solvents such as ethyl ether, but insoluble in petroleum ether: divalent copper (red-violet), and divalent iron (green). The complexes with palladium (green), cobalt (gray-brown) and trivalent iron (brown) are distinguished from the other complexes by their extractability by petroleum ether. The solutions are stable for some hours.

Regulation of the pH is very important in work with *o*-nitrosophenol. If the acidity is too high the complexes are not quantitatively formed. On the other hand if the acidity is too low, a mixture of two compounds is

<sup>44</sup> G. Cronheim, *Ind. Eng. Chem., Anal. Ed.*, **14**, 445 (1942).

<sup>45</sup> For preparation see O. Baudisch, *J. Am. Chem. Soc.*, **63**, 622 (1941).

said to be formed in the case of the water-soluble compounds:



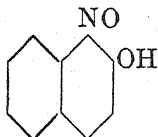
and



in which Np is the *o*-nitrosophenol radicle. Compound (1) is soluble only in water, compound (2) in certain organic solvents such as ethyl ether.

Methods have been worked out for the determination of cobalt<sup>44</sup> and ferrous iron.<sup>46</sup> In the determination of the former the aqueous solution is adjusted to pH 4 with a citrate buffer and shaken with a petroleum ether solution of reagent to bring the cobalt into the ether phase; citrate (or tartrate) prevents the reaction of iron, provided too much of the latter is not present. For the determination of ferrous iron, the aqueous solution of pH 5.1–5.3 is shaken with a petroleum ether solution of reagent and the green color of the aqueous phase compared or measured.

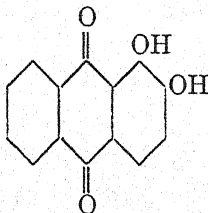
#### VII. $\alpha$ -Nitroso- $\beta$ -Naphthol



This reagent forms slightly soluble internal complexes with a number of metals, but these have been investigated only slightly from the standpoint of colorimetric analysis. Cobalt may be determined colorimetrically by dissolving the washed precipitate of cobalt nitroso-naphtholate in chloroform.<sup>47</sup> The ferrous complex can be extracted with chloroform (strong green color). The use of  $\alpha$ -nitroso- $\beta$ -naphthol is rendered somewhat unattractive by its intense color, which moreover is quite similar (brownish) to that of most of the complexes it forms.

**Nitroso-R-salt** (1-nitroso-2-hydroxy-3,6-naphthalene disodium sulfonate) is a most important colorimetric reagent for the determination of cobalt (p. 201), but it has also been used for determining ferrous iron, with which it yields a green color in basic medium.<sup>48</sup> Copper and nickel give strong yellow-brown colors with the reagent at a pH less than 7.

#### VIII. Alizarin



<sup>46</sup> G. Cronheim, *Ind. Eng. Chem., Anal. Ed.*, **14**, 447 (1942).

<sup>47</sup> L. Waldbauer and N. M. Ward, *Ind. Eng. Chem., Anal. Ed.*, **14**, 727 (1942).

<sup>48</sup> C. P. Sideris, *Ind. Eng. Chem., Anal. Ed.*, **14**, 756 (1942).

Alizarin (1, 2-dihydroxyanthraquinone), or alizarin S (sodium alizarin sulfonate), forms slightly soluble, strongly colored lakes with most cations at proper acidities. The zirconium lake is formed in solutions of fairly high acidity and is made the basis of a sensitive method for the determination of zirconium (p. 461). The most common colorimetric method for the determination of fluorine depends upon the bleaching of the red color of the zirconium-alizarin S lake by traces of fluoride as a consequence of the formation of slightly dissociated complex zirconium fluoride. Alizarin S is also used for the determination of aluminum (p. 126).

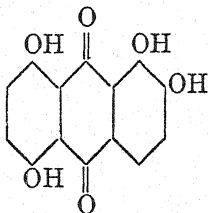
With the exception of quinalizarin, other hydroxyanthraquinones have found little application in colorimetric analysis. Purpurin has been used in the determination of zirconium (p. 462). Hydroxyanthraquinones with an OH group in the ortho position are stated to give sensitive color reactions with stannic tin.<sup>49</sup> One of the most suitable of these is 1, 2, 7-trihydroxyanthraquinone.

### 1-Amino-4-hydroxyanthraquinone

An alcoholic solution (0.1 per cent) of this compound produces a purple colloidal precipitate with thorium in weakly acid solution (pH 2) which shows a reddish fluorescence in ultraviolet light.<sup>50</sup> The sensitivity is low, approximately 1:125000.

Gallium and praseodymium also fluoresce under these conditions but not as strongly as thorium (0.1 mg. Th  $\equiv$  1.5 mg. Ga  $\equiv$  10 mg. Pr). Zirconium and iron (III) decrease the thorium fluorescence, and cerium (IV), silver, gold, and mercury (I) as well as metals of the platinum group are stated to destroy the reagent. Phosphate, fluoride, and sulfate in small amounts destroy the thorium fluorescence.

### Quinalizarin (1,2,5,8-tetrahydroxyanthraquinone)



This dye dissolves in alkalis to give a violet solution which is turned yellow by acids. It is also soluble in alcohol, acetone, etc. Quinalizarin has been used for the colorimetric determination of beryllium, gallium,

<sup>49</sup> E. Eegriwe, *Z. anal. Chem.*, **120**, 81 (1940).

<sup>50</sup> C. E. White and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.*, **13**, 809 (1941).

magnesium, aluminum and boron, and for the detection of germanium<sup>51</sup> and the rare earths.<sup>52</sup>

The addition of quinalizarin to a sodium hydroxide solution containing beryllium gives a blue color which is quite different from the violet color obtained in the absence of beryllium.<sup>53</sup> Aluminum does not react in the strongly basic solution. A method for the determination of beryllium has been based on this behavior by Fischer.

Gallium at pH 4.5 to 6 yields a pink to amethyst color with quinalizarin, and Willard and Fogg<sup>54</sup> have worked out a quantitative method for the element with this reagent (p. 236).

Magnesium hydroxide adsorbs quinalizarin and gives a blue lake.<sup>55</sup>

In faintly acid solution aluminum produces a violet color due to lake formation.<sup>56</sup>

In strong sulfuric acid, boric acid gives a blue color with quinalizarin which is due to the formation of an internal complex boronhydroxyanthraquinone compound.<sup>57</sup> Columbium and tantalum also react in sulfuric acid medium (p. 213).

Many metals will react with quinalizarin in slightly acid medium, giving color changes. Thus at pH 5, iron (III) and lead produce a blue color, tin (II), antimony (III), copper (II), indium (III), germanium, vanadium (IV and V), and molybdenum (VI) a pink color. These reactions are not prevented by the addition of fluoride. The following metals also react at pH 5 but fluoride prevents the reaction: zirconium, thorium, rare earths (all blue colors); tin (IV), beryllium, aluminum, thallium (III), titanium (IV), arsenic (III), antimony (V) (all pink colors). The alkalis, alkaline earths, magnesium, manganese, iron (II), mercury (II), thallium (I), cadmium, uranium (V), and tungsten (VI) give rise to no color at pH 5, while other metals such as silver, mercury (II), bismuth, tantalum, etc. are precipitated as chlorides or hydrolyzed out.<sup>58</sup>

<sup>51</sup> A. S. Komarovskiy and N. S. Poluektov, *Mikrochemie*, **18**, 66 (1935).

<sup>52</sup> A. S. Komarovskiy and I. M. Korenman, *Z. anal. Chem.*, **94**, 247 (1933).

<sup>53</sup> H. Fischer, *Wiss. Veröffent. Siemens-Konzern*, **5**, 99 (1926); *Z. anal. Chem.*, **73**, 54 (1928).

<sup>54</sup> H. H. Willard and H. C. Fogg, *J. Am. Chem. Soc.*, **59**, 40 (1937).

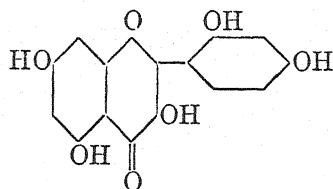
<sup>55</sup> F. L. Hahn, H. Wolf, and G. Jäger, *Ber.*, **57**, 1394 (1924). F. L. Hahn, *Mikrochemie (Pregl-Festschrift)*, **1929**, p. 127.

<sup>56</sup> I. M. Kolthoff, *Chem. Weekblad*, **24**, 447 (1927); *J. Am. Pharm. Assoc.*, **17**, 260 (1928).

<sup>57</sup> F. Feigl, *Specific and Special Reactions*. Nordeman, New York, 1940; pp. 41, 126; G. S. Smith, *Analyst*, **60**, 735 (1935); K. C. Berger and E. Truog, *Ind. Eng. Chem., Anal. Ed.*, **11**, 540 (1939).

<sup>58</sup> The material in this paragraph is taken from H. H. Willard and H. C. Fogg, *J. Am. Chem. Soc.*, **59**, 40 (1937).

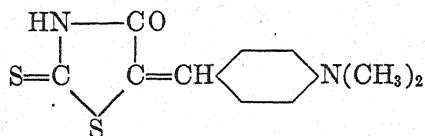
IX. Morin



In weakly acid (acetic acid-acetate) solution morin reacts with aluminum, scandium, beryllium, gallium, and indium to give compounds that show strong fluorescence (especially in ultra violet light). Scandium is said to give a fluorescence in weak mineral acid solution also.<sup>59</sup> The rare earths show a weak fluorescence. The determination of aluminum by its fluorescence with morin has been described.<sup>60</sup> Fluoride, phosphate, arsenate and even sulfate interfere by reducing the fluorescence intensity.

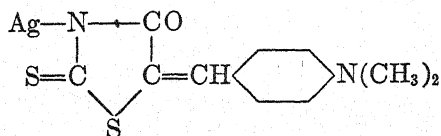
In strongly basic solution (1 *N* in sodium hydroxide) morin becomes nearly a specific reagent for beryllium. Aluminum, gallium, and indium no longer react in strongly basic medium. Zinc, however, fluoresces, but cyanide prevents its interference. Lithium fluoresces very weakly. Calcium can be prevented from interfering by addition of pyrophosphate. For further details see p. 152.

X. *p*-Dimethylaminobenzylidenerhodanine



This reagent gives slightly soluble red or violet precipitates in acid solution with silver, mercury (I and II), cuprous copper, gold, and palladium. Platinum (IV) also reacts, but not very sensitively. Many other metals react in alkaline solution. The reagent has been recommended by Feigl for the detection of the metals mentioned.

The compound formed with silver has the formula:



<sup>59</sup> G. Beck, *Mikrochim. Acta*, **2**, 9 (1937).

<sup>60</sup> C. E. White and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.*, **12**, 229 (1940).

and it seems likely that the cuprous and mercurous compounds have similar formulas. According to Feigl the palladium compound is probably a chloro addition product with the rhodanine.

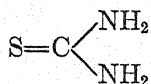
Dimethylaminobenzylidenerrhodanine has been used for the colorimetric determination of silver (p. 395),<sup>61</sup> mercury,<sup>62</sup> and gold.<sup>63</sup> The reagent is used in the form of an acetone solution. Since the colored reaction products are very slightly soluble, the reagent is not an ideal one for colorimetry. However, in very dilute solutions the colloidal suspension is fairly stable, and in less dilute solutions it can be made so by the addition of a suitable protective colloid.

Minute amounts of palladium—as little as 0.1  $\gamma$ —can be determined in 0.02 *N* hydrochloric acid solution. Small amounts of silver give no color in the hydrochloric acid medium. Gold, however, reacts with a sensitivity approaching that of palladium and this is a serious objection to the practical use of the rhodanine for the determination of palladium. The reaction of gold can not be prevented by the addition of complex-forming reagents without destruction of the color given by palladium. For this reason nitrosodiphenylamine is generally a better reagent for palladium (p. 353).

## XI. Tannic Acid

This reagent is better known as a metal precipitant than as a colorimetric reagent, but as the latter it may at times find some application, since in faintly acid solutions it gives fairly sensitive reactions with titanium (red-orange), vanadium (blue), molybdenum (reddish), and iron (bluish, turning red with ammonia). All of these metals yield precipitates above a minimum concentration. Uranium (VI) gives a brown color, and a colorimetric method based upon this reaction has been described.<sup>64</sup>

## XII. Thiourea



In acid solutions thiourea<sup>65</sup> produces a yellow color with bismuth and palladium. Antimony gives a slight color with the reagent, and silver,

<sup>61</sup> I. C. Schoonover, *J. Research Natl. Bur. Standards*, **15**, 377 (1935).

<sup>62</sup> N. Strafford and P. F. Wyatt, *Analyst*, **61**, 523 (1936).

<sup>63</sup> B. K. Merejkovsky, *Bull. soc. chim. biol.*, **15**, 1336 (1933).

<sup>64</sup> P. N. Das Gupta, *J. Indian Chem. Soc.*, **6**, 763 (1929).

<sup>65</sup> J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.*, **14**, 435 (1942), found that some substituted thioureas gave slightly more sensitive reactions than thiourea with bismuth. Benzidinedithiourea gives a sensitivity about four times as great as that given by thiourea.

platinum and mercury give precipitates. Selenite is reduced to red selenium.

A hydrochloric acid solution of osmium (as  $\text{OsO}_4$  or  $\text{OsCl}_6^-$ ) heated with thiourea becomes red owing to the formation of  $\text{Os}(\text{NH}_2\cdot\text{CS}\cdot\text{NH}_2)_6\text{Cl}_3\cdot\text{H}_2\text{O}$ .<sup>66</sup> The reaction is applicable to the determination of traces of osmium. Ruthenium gives a blue color under the same conditions.

### XIII. Thiocyanate

An alkali metal thiocyanate alone or in conjunction with other reagents is a colorimetric reagent for ferric iron, molybdenum, rhenium, tungsten, cobalt, and bismuth. The red compound given by thiocyanate ion in acid solution with ferric ion has been assigned various formulas. Recent work<sup>67</sup> tends to show that the color is due to the ion  $\text{FeCNS}^{++}$ . The reaction is a sensitive one and provides a good method for the determination of ferric iron in spite of the pronounced effect of such factors as thiocyanate concentration and the time of standing on the color intensity.

Molybdate with thiocyanate yields an amber to red solution when treated with a reducing agent such as stannous chloride. The colored compound contains molybdenum in the quinquevalent state and may have the formula  $\text{MoO}(\text{CNS})_3$ . Rhenium (VII) gives a similar color under the same conditions, perhaps due to  $\text{ReO}(\text{CNS})_4$ . The colored compounds can be extracted with ether, and the interference of various colored foreign ions thus eliminated.

Under special conditions tungsten (VI) will give a strongly colored soluble yellow compound when treated with thiocyanate and a strong reducing agent such as stannous chloride or titanous chloride. The colored compound is soluble in ether.

In neutral or slightly acid solution containing 50 per cent of acetone, thiocyanate produces a blue color with cobalt which is possibly due to some such ion as  $\text{Co}(\text{CNS})_4^-$ . The reaction is fairly sensitive and specific (a reducing agent such as stannous chloride prevents interference of iron and copper in small amounts).

A comparatively high concentration of an alkali thiocyanate will give a yellow color with bismuth. The reaction is not very sensitive and usually of little value in trace analysis.

#### Thiocyanate and Pyridine

These reagents give precipitates with cupric, cadmium, zinc, nickel, cobalt and other metal ions. These precipitates are soluble in chloroform;

<sup>66</sup> L. Chugaev, *Compt. rend.*, **167**, 235 (1918).

<sup>67</sup> H. E. Bent and C. L. French, *J. Am. Chem. Soc.*, **63**, 568 (1941); S. M. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941); R. K. Gould and W. C. Vosburgh, *ibid.*, **64**, 1631 (1942).

the copper compound,  $\text{Cu}(\text{CNS})_2 \cdot 2 \text{ Py}$ , gives a green solution, the nickel compound,  $\text{Ni}(\text{CNS})_2 \cdot 4 \text{ Py}$ , a blue, and the cobalt compound,  $\text{Co}(\text{CNS})_2 \cdot 4 \text{ Py}$ , a pink solution. The Biazzo<sup>68</sup> method for copper involves extraction of the copper compound with chloroform and comparison or measurement of the color of the latter. This method has now been supplanted by others (p. 217). Occasionally traces of the metals mentioned are isolated by extraction of their pyridine-thiocyanate complexes preparatory to determination by other methods.

#### XIV. Halogen Acids

##### Hydrochloric Acid

Strong hydrochloric acid forms chloro acids with a number of metals and some of these are strongly colored, especially those with ferric iron (yellow), copper (yellow), cobalt (blue), iridium (brown) and rhodium (rose-red). Hydrochloric acid has been employed as a colorimetric reagent for these metals, but the sensitivity is inferior to that of other methods (except for iridium) and such metals as platinum, palladium, gold, ruthenium, nickel, and others interfere by giving more or less strong colors.

Copper (II) gives the maximum color intensity with hydrochloric acid when the acid concentration is 28 per cent or higher.<sup>69</sup> Iron interferes seriously since, weight for weight, it produces twice as strong a color as copper. The coloration given by cobalt is much less intense than that of copper.

Chloroplatinous acid, obtained by reduction of chloroplatinic acid with stannous chloride, is an important determination form of platinum (p. 358).

##### Hydrobromic Acid

Bromide ion in acid solution gives strongly colored (yellow, brown, etc.) complexes with iron (III), copper (II),<sup>70</sup> platinum (IV), and gold (III). Bromauric acid is easily extracted from aqueous solution by ethyl acetate.

##### Hydriodic Acid

Iodide ion in excess yields strongly colored soluble complexes in acid solution with bismuth (iodobismuthous acid, yellow), quadrivalent platinum ( $\text{PtI}_4$ , brownish red), and palladium ( $\text{PdI}_4$ , brown). The reaction with bismuth is the basis of one of the most sensitive methods for the colorimetric determination of this element. The formation of iodoplatinic acid is applied not only in the determination of platinum but also in the indirect determination of potassium after precipitation as chloroplatinate.

It may be mentioned that the iodide reaction with antimony (III) is

<sup>68</sup> R. Biazzo, *Ann. chim. applicata*, **16**, 96 (1926).

<sup>69</sup> C. Hüttner, *Z. anorg. Chem.*, **86**, 351 (1914).

<sup>70</sup> G. Denigès and E. Simonot, *Bull. soc. pharm. Bordeaux*, **54**, 337 (1914).



very sensitive if a high concentration of iodide is used but the difficulty of reducing the free iodine formed by air-oxidation under these conditions makes the reaction difficult to apply. Indirectly iodide may be used for the determination of thallium by liberation of iodine by reaction with thallic salts, the free iodine being determined colorimetrically after extraction with an organic solvent (p. 409). Calcium may also be determined indirectly after oxidation of the oxalate with ceric salt (p. 179).

### XV. Ammonium Hydroxide

Ammonia in excess gives fairly strong colors with copper (II), nickel, and trivalent cobalt (rose-pink)<sup>71</sup> and has been used for the determination of these metals. The sensitivity, however, is inferior to that of other methods so that ammonia is not an important colorimetric trace reagent, although it may render good service when larger amounts of these metals are to be determined.

### XVI. Hydrogen Peroxide

In acid solution hydrogen peroxide produces a yellow color with titanium (IV), a reddish brown with vanadium (V), and a yellow with molybdenum (VI). The reaction with titanium is very sensitive and is the basis of the most generally useful colorimetric method for this element (p. 420). Vanadium also can be determined by the hydrogen peroxide method. The color given by titanium can be destroyed by adding hydrofluoric acid but the vanadium color is not affected.

In a mixture of strong sulfuric and phosphoric acid, containing 40 per cent of the latter, hydrogen peroxide may be used to determine columbium (yellow coloration) in the presence of small amounts of titanium, the color of the latter being repressed by the phosphoric acid.<sup>72</sup> Tantalum gives no color.

A colorimetric method has been described for the determination of molybdenum by the formation of permolybdate (reddish brown) in alkaline solution with hydrogen peroxide.<sup>73</sup> Uranium and cerium give fairly intense yellow colors in basic medium (p. 436 and p. 188). The reaction with molybdenum is of slight importance, but those with uranium and cerium are of practical value.

### XVII. Molybdate and Reducing Agents

The heteropoly molybdic acids formed when molybdate reacts in acid solution with phosphate, arsenate, silicate, and germanate may be made the

<sup>71</sup> B. S. Evans, *Analyst*, **50**, 389 (1925).

<sup>72</sup> G. Thanheiser, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, **22**, 255 (1940).

<sup>73</sup> A. D. Funck, *Z. anal. Chem.*, **68**, 283 (1926).

basis of sensitive methods for the determination of these ions. In the case of germanium and silicon the corresponding molybdic acids may be used directly in the method; germanomolybdic and silicomolybdic acids yield moderately strongly colored yellow solutions. As is well known, the heteropoly molybdic acids are more easily reduced than molybdic acid itself, so that it is possible to determine phosphate, silicate, arsenate and germanate by treating the acid solution of these ions with ammonium molybdate and a suitable reducing agent. Under the proper conditions only the molybdenum combined with the ions mentioned will be reduced to a lower valence to give the intensely colored "molybdenum blue." The blue reduction product has a variable composition and its constitution is uncertain.

Many reducing agents have been used in ceruleomolybdate methods. For the determination of phosphate, stannous chloride and certain organic reducing agents such as 1-amino-2-naphthol-4-sulfonic acid and hydroquinone are widely used. Hydrazine sulfate is very suitable for the reduction of arsenomolybdate in boiling solution and may be used as well for phosphomolybdate. For the reduction of germanomolybdate ferrous sulfate has been employed. A study has been made by Woods and Mellon<sup>74</sup> of the molybdenum blue method for the determination of phosphorus, silicon, and arsenic, and reference should be made to this paper for results obtained with a number of reducing agents.

### XVIII. Hydrogen Sulfide

Under proper conditions hydrogen sulfide (or a soluble sulfide) can be used to produce a colloidal suspension of various heavy metal sulfides suitable for photometric measurement or comparison. In most cases dithizone can be substituted for sulfide with advantage because of higher sensitivity and greater selectivity.

### XIX. Oxidizing and Reducing Agents

Many organic compounds can be oxidized to strongly colored products in inorganic systems of high oxidation potential, and sometimes colorimetric methods of practical value can be based on these reactions. Such methods are likely to be lacking in specificity and must be applied with caution.

Another drawback of these methods is the frequent poor stability of the colored organic product. A few methods of this type may be mentioned. Benzidine gives a fugitive blue-green color with permanganate in acid solution and a blue color with quadrivalent iridium. *o*-Tolidine in acid solution is oxidized by auric gold to a yellow product; many other strong oxidizing agents produce the same color. Lead has been determined by

<sup>74</sup> J. T. Woods and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 760 (1941).

anodic deposition of the dioxide, followed by solution of the latter in an acetic acid solution of tetramethyldiaminodiphenylmethane to give a blue diphenylmethane dye. The leuco base of malachite green may be used for determining gold and iridium; tetramethyl-p-phenylenediamine has been recommended as a reagent for osmium. Diphenylamine has been used for the colorimetric determination of vanadium (V).<sup>75</sup> Phenolphthalin (obtained by reduction of phenolphthalein with zinc in sodium hydroxide solution) together with hydrogen peroxide gives a pink color with the most minute amounts of copper.

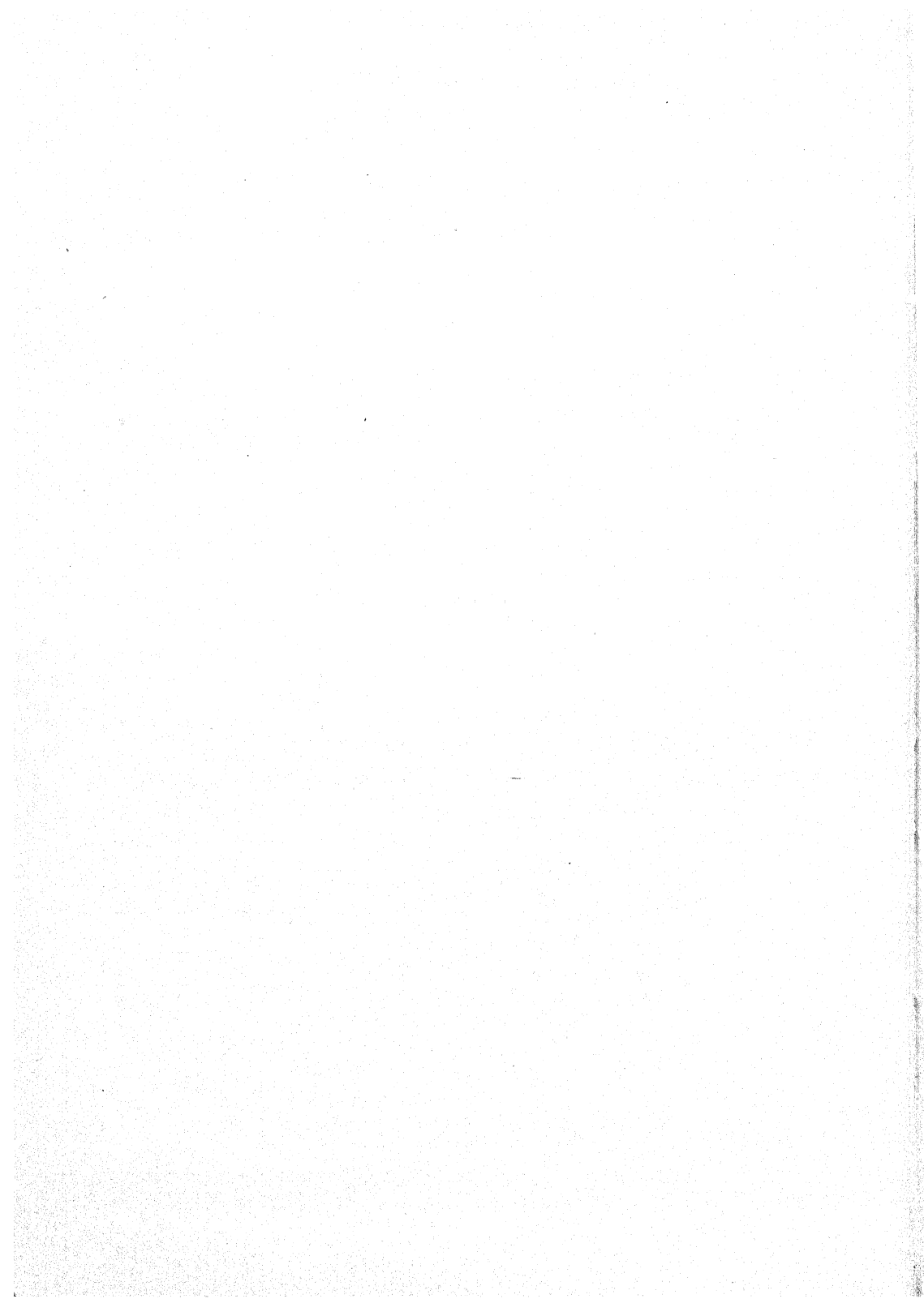
The reduction of an organic compound to a strongly colored product by an inorganic substance is rarely applied in colorimetry. Cacotheline, the nitro compound of brucine, is reduced by stannous tin and other strong reducing agents<sup>76</sup> to a soluble violet-colored substance. This reaction is used for the detection of tin, but has not been applied quantitatively.

Inorganic reagents which are oxidized or reduced to strongly colored substances find considerable use in the indirect determination of metals. Thus iodide may be employed for the determination of ceric cerium, and thallium as well as calcium. Either the brown tri-iodide ion or the blue iodine-starch product may be made the basis of these methods. Reference has already been made to the use of ammonium molybdate in molybdenum blue methods and the use of phosphotungstomolybdic acid for the determination of many metals precipitated as oxinates or thionolates. The latter reagent is also reduced by certain metals in their lower valence states, as for example antimony (III).

In a different class are oxidizing and reducing agents which convert metals into colored products. For example persulfate at 100° in the presence of a little silver as catalyst oxidizes manganese, chromium and cerium to their strongly colored highest valence states. On the other hand, stannous chloride is a valuable reagent for the determination of gold, tellurium, platinum and rhodium by reduction to the colloidal metal or lower valence state, as well as for the determination of other metals in conjunction with other reagents as we have already seen.

<sup>75</sup> For the mechanism of the color change in the oxidation of diphenylamine and some of the other compounds mentioned above, consult the section on redox indicators, pp. 105-141, in I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. I. Interscience, New York, 1942.

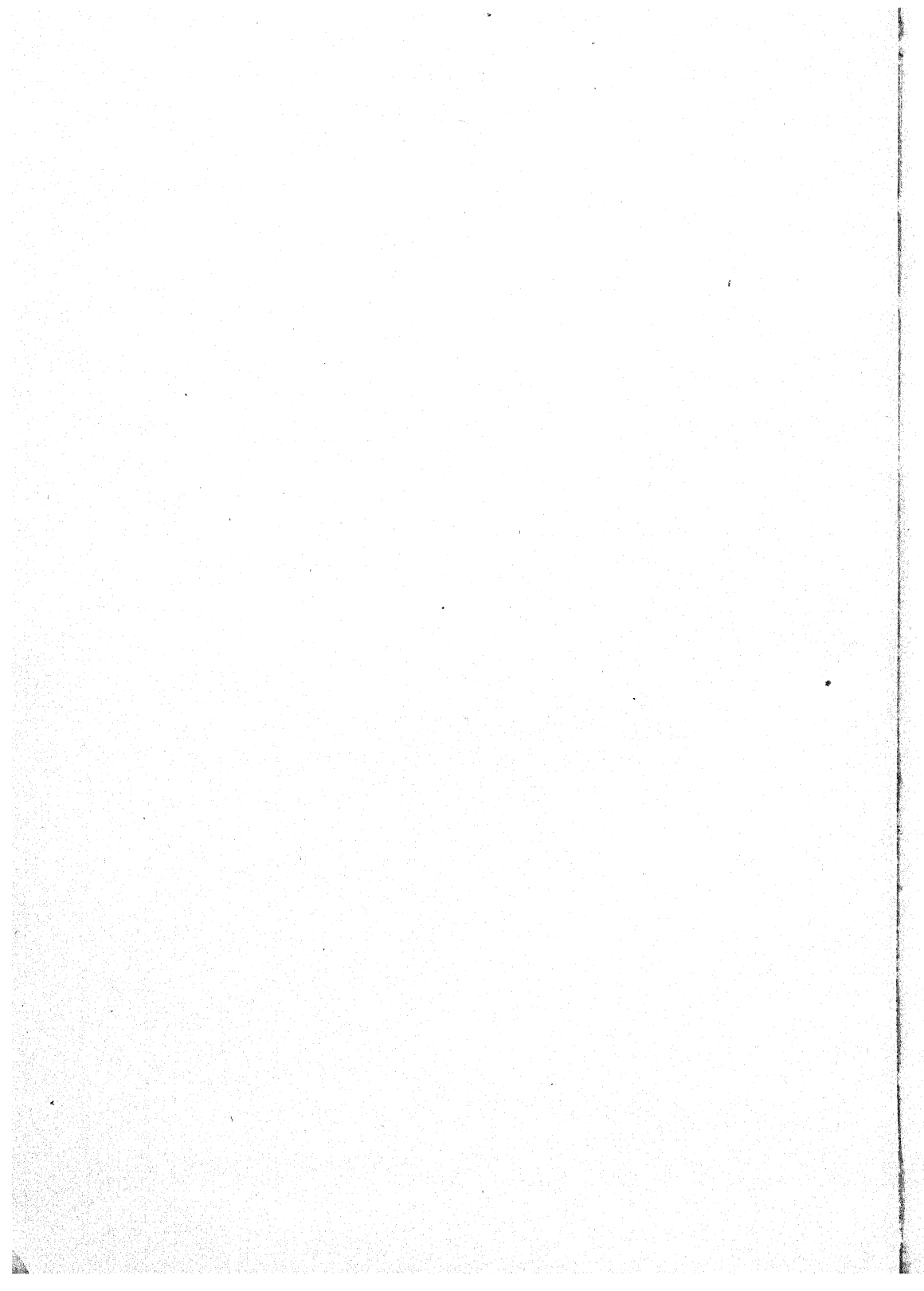
<sup>76</sup> L. Rosenthaler, *Mikrochim. Acta*, **3**, 190 (1938)



**SPECIAL PART**

**PROCEDURES FOR THE**

**DETERMINATION OF TRACES OF METALS**



## EXPLANATORY NOTES

The plan of treatment is the following. First the separation of the metal in question from other elements is considered, chief attention being given so far as possible to those likely to interfere in the colorimetric determination and to those frequently associated with the metal in question. For many metals, methods worked out specifically for the separation of traces are lacking and a brief general outline of separations is all that can be given, with the hope that some of these separations can be extended with suitable modifications to work involving small quantities. Next the important methods of determination are described. The procedures are given in general form so far as possible, independent of the nature of the original sample. The effect of foreign elements, so far as known, is mentioned. Finally, for many of the more important trace elements, directions are given for the determination of the metal in important classes of material. To a large extent these procedures pertain to the preparation of the sample and the isolation of the metal; the final determination is usually made according to the preceding general procedure but in some instances the nature of the sample makes it advisable to give special directions for the final determination. The materials considered include silicate rocks, which are of great scientific interest and which in great measure serve as models for other samples, and biological materials in general.

Directions in most of the procedures assume the use of some form of a photoelectric photometer, but often very little change need be made when other photometers or a color comparator of the Duboscq type is to be employed. The table of sensitivities on p. 38 should be of some aid in decisions regarding suitable concentrations of the colored substance for measurement. The use of rather weakly colored solutions obtained from relatively small samples is frequently called for in the procedures in order that the analysis may thus be expedited; the highest degree of relative precision in color intensity measurement is usually not required in trace analysis. Standard curves are given for some of the procedures with the purpose of indicating the sensitivity of the method, the reproducibility, and, sometimes, adherence to Beer's law. These curves were for the most part obtained with a filter photometer and do not necessarily reflect the best optical methods of measurement; in some cases a more selective filter or the use of a spectrophotometer will give much greater sensitivity as well as closer conformity to Beer's law. Since the concentration-extinction curves are intended primarily for trace analysis, they have been restricted to low concentrations.

## CHAPTER V

### ALUMINUM

#### I. Separations

From magnesium and the alkaline earth metals, aluminum can be separated by precipitation with ammonium hydroxide in the presence of an ammonium salt. A few milligrams of zirconium or ferric iron should be added to gather the aluminum. If iron is used as collector it must later be separated, since it interferes in all the colorimetric methods for the determination of aluminum. Only a slight excess of ammonia should be added (pH 7-7.5). If chromium is first oxidized to the hexivalent state it is readily separated from aluminum in the ammonia precipitation.

Separation of traces of aluminum from other metals by the precipitation of the latter with an excess of sodium hydroxide is a dubious method because of the coprecipitation of aluminum with the metal hydroxides, which is especially marked with magnesium and nickel hydroxides. The method may be of some use when the amount of the precipitated hydroxides is small; a double precipitation should be made. Sodium hydroxide precipitation is often used to separate iron, but the precipitation of the latter is not entirely complete.<sup>1</sup> Better results can be obtained in separating aluminum from a number of metals if a mixture of sodium hydroxide and sodium sulfide (a solution containing 10 per cent of each) is used instead of sodium hydroxide alone. Aluminum is less strongly adsorbed on the metal sulfides than on the corresponding hydroxides (as of iron and manganese). A small amount of copper may be added to aid in obtaining a better filterable precipitate of iron sulfide (low concentrations of iron tend to give a green colloidal solution). Precipitation should be made in hot solution followed by digestion. Account must be taken of the introduction of aluminum from the glassware (platinum should preferably be used) or from the reagents.

Aluminum may be precipitated as phosphate in weakly acid medium, with ferric phosphate as collector, and thus separated from such metals as calcium and magnesium whose phosphates are not precipitated under these conditions. This method is frequently applied in isolation of aluminum from the ash of biological materials (p. 125). A small amount of phosphate does not interfere in the usual colorimetric method for aluminum (p. 118).

<sup>1</sup> W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*. Wiley, New York, 1929; p. 400. The trace of iron that remains in solution can be largely removed by filtration through paper (adsorption by cellulose).



Cupferron precipitation in 1:10 sulfuric acid solution serves to separate ferric iron, zirconium, titanium, vanadium, tin, and some other elements less frequently encountered, from aluminum. Ferric cupferrate can be extracted with a mixture of ether and benzene (p. 126). Excess cupferron in the filtrate or in the extracted solution can be destroyed by heating with sulfuric and nitric acids.

A very useful method for eliminating many metals at one stroke involves electrolysis with a mercury cathode in dilute sulfuric acid solution. Large quantities of the following elements can thus be separated from aluminum: iron, copper, nickel, cobalt, zinc, gallium, germanium, silver, cadmium, indium, tin, antimony, chromium, molybdenum, lead, bismuth, arsenic, selenium, tellurium, mercury, thallium, rhenium, gold, and the platinum

TABLE 13  
ISOLATION OF ALUMINUM BY PRECIPITATION WITH PHOSPHATE  
IN THE PRESENCE OF IRON<sup>a</sup>

Al added $\gamma$	Al found $\gamma$	Al recovered $\gamma$
0	5.0	
0	5.2	
1	6.3	1.3
1	5.9	0.9
5	10	5
5	12	7
30	35	30
30	37	32
50	57	52
50	54	49

<sup>a</sup> Conditions as in the procedure on p. 125.

Figures from J. Cholak, D. M. Hubbard, and R. V. Story, *Ind. Eng. Chem., Anal. Ed.*, 15, 57 (1943).

metals (except ruthenium). Manganese is only partially removed, but the amount remaining usually does not interfere in the aurintricarboxylate method. Elements remaining in solution with aluminum include beryllium, vanadium, phosphorus, magnesium, the alkaline earth metals, and the rare earth metals. The procedure is described on p. 124.

Minute amounts of aluminum can be separated from beryllium, magnesium, and the alkaline earth metals by extraction of the 8-hydroxyquinolate salt with chloroform from a solution having a pH of about 4.5. Many other metals, including ferric iron, are simultaneously extracted, so that the method has limited applicability.

Large amounts of ferric iron can in great measure be removed by extraction of a 1:1 hydrochloric acid solution with ethyl ether. Small quantities

of ferric iron have been removed by extraction of the thiocyanate with amyl alcohol.<sup>2</sup>

## II. Methods of Determination

The direct colorimetric determination of aluminum is based on the formation of a strongly colored lake with a suitable organic reagent. The exact nature of the lakes produced is uncertain. They have been regarded as internal complexes of aluminum which exist in colloidal solution or as colloidal aluminum hydroxide on which the organic compound is adsorbed in one fashion or another with a pronounced change in color. There are many organic substances that can be used in this manner. Some of the more common reagents are ammonium aurintricarboxylate, sodium alizarin sulfonate (alizarin S), eriochromecyanin and hematoxylin. No one of these is so markedly superior that it eliminates the others from consideration. Aurintricarboxylate is much used in the U. S. A., whereas alizarin sulfonic acid and eriochromecyanin have found greater favor in Europe. Control of the pH of the solution is an important factor in all of these methods. Iron interferes badly.

The indirect colorimetric determination of aluminum is founded on its precipitation as the 8-hydroxyquinolate, which after washing is dissolved in acid and the 8-hydroxyquinoline determined by conversion into an azo dye or in some other way.

Aluminum gives a strongly fluorescent compound with morin in weakly acid solution. The reaction is indeed very sensitive but for general use it has no advantages over colorimetric reactions.

For a comparative study of various colorimetric methods for the determination of aluminum see a paper by Schams.<sup>3</sup>

### A. THE AURINTRICARBOXYLATE METHOD<sup>4</sup>

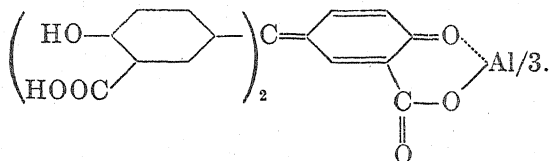
A dilute neutral or weakly acid solution of ammonium aurintricarboxylate (aluminon) has a yellow-brown color, which becomes pale yellow when the solution is made basic; addition of mineral acid precipitates aurintricarboxylate.

<sup>2</sup> A. P. Musakin, *Z. anal. Chem.*, **105**, 351 (1936); *Zavodskaya Lab.*, **9**, 507 (1940). The slightly acid sample solution is treated with sufficient potassium thiocyanate to make its concentration about 10 per cent, and the solution is extracted with one-fourth its volume of amyl alcohol until the latter no longer shows a pink color.

<sup>3</sup> O. Schams, *Mikrochemie*, **25**, 16 (1938).

<sup>4</sup> J. A. Scherrer and W. D. Mogeran, *J. Research Natl. Bur. Standards*, **21**, 105 (1938); O. B. Winter, W. E. Thrun, and O. D. Bird, *J. Am. Chem. Soc.*, **51**, 2721 (1929); P. S. Roller, *ibid.*, **55**, 2437 (1933); G. E. F. Lundell and H. B. Knowles, *J. Ind. Eng. Chem.*, **18**, 60 (1926); J. H. Yoe and W. C. Hill, *J. Am. Chem. Soc.*, **49**, 2395 (1927); V. C. Myers, J. W. Mull, and D. B. Morrison, *J. Biol. Chem.*, **78**, 595 (1928); D. F. Eveleth and V. C. Myers, *ibid.*, **113**, 449 (1936); K. B. Lehmann, *Arch. Hyg.*, **106**, 309 (1931).

carboxylic acid.<sup>5</sup> In weakly acid (acetate-acetic acid buffer) or neutral medium the reagent gives a deep red color with minute amounts of aluminum. The red color has been ascribed by Feigl to an internal complex salt having the formula:



In some procedures the color thus produced in acid medium is compared or measured without further ado, whereas in others the solution is made basic with ammonia before comparison. The writer concurs in the recommendation of Roller (*loc. cit.*) and others<sup>6</sup> that the determination be carried out in weakly acid solution. The advantages in making the solution basic after developing the color in acid medium are stated to be the weaker color of the excess reagent in basic medium and the possibility of reducing the interference of certain metals such as chromium. On the other hand the sensitivity of the reaction is diminished in basic medium, the lake then becomes less stable, and the precipitation of various metals takes place. Furthermore, the addition of ammonia must be made under controlled conditions to obtain reproducible results in the basic medium procedure.

### 1. Determination in Acid Medium

The procedure given below (p. 120) has been found to give reproducible results, and is very simple to carry out. The solution is adjusted to neutrality, a definite amount of hydrochloric acid is added to assure the presence of aluminum in the ionic form, and after addition of reagent, the pH is brought to about 5.5 with ammonium acetate. The color intensity increases slowly after the initial rapid rise; readings can be made after 15-30 minutes. The relation between aluminum concentration and extinction is shown in Fig. 20. The sensitivity is very great as can be seen from the curve. The visual sensitivity also leaves little to be desired. By using 0.25 ml. of 0.2 per cent solution of the aurintricarboxylate in 10 ml. of

<sup>5</sup> The quality of the ammonium aurintricarboxylate is a factor of importance in the success of the colorimetric method. According to J. A. Scherrer and W. H. Smith, *J. Research Natl. Bur. Standards*, **21**, 113 (1938), some products on the market are not satisfactory because they are too strongly colored, yield unstable solutions, or produce "muddy" precipitates. A satisfactory product can be prepared according to directions given by these authors, and is, moreover, commercially available.

<sup>6</sup> A. P. Musakin, *Zavodskaya Lab.*, **9**, 507 (1940); L. M. Kul'berg and E. I. Rovinskaya, *ibid.*, **9**, 145 (1940); A. K. Babko, *J. Applied Chem. U. S. S. R.*, **12**, 560 (1939).

sample, as little as 0.01  $\gamma$  of aluminum can be detected in a column of solution having a cross section of 1 square centimeter.

The effect of foreign elements has not been investigated with reference to the particular pH existing in the final solution in this procedure, but the effect found by Roller<sup>4</sup> in a similar method at a slightly higher pH of 6.3

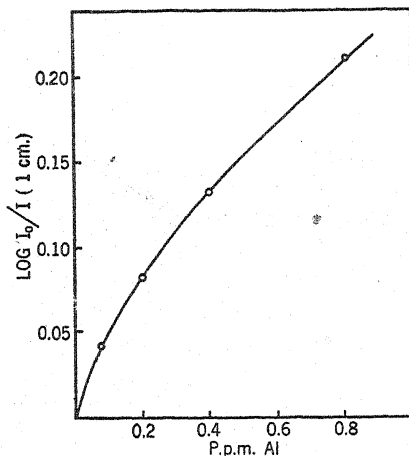


Fig. 20.—Determination of aluminum with aurintricarboxylate according to Procedure 1. Extinction determined after 15 minutes; green filter (Cenco No. 2).

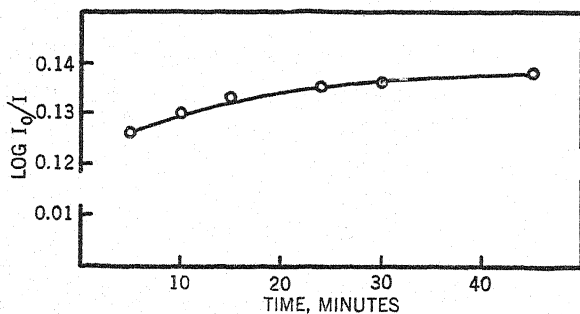


Fig. 21.—Color intensity as a function of time in the aurintricarboxylate method for aluminum (0.4 p.p.m. of Al). Determination in weakly acid solution according to Procedure 1.

may be mentioned as indicating what may be expected. He found that 10 mg. of barium, calcium, magnesium, zinc, lead; 0.1 mg. of cobalt and copper; and 5 mg. of  $\text{PO}_4^{=}$ , all in a volume of 18 ml., gave no color. One-tenth of a milligram of chromium ion (green form) gave as much color as 0.0005 mg. of aluminum (after 15 minutes standing), and 0.01 mg. of ferric iron as much color as 0.005 mg. of aluminum.

## 2. Determination in Basic Medium

Scherrer and Mogerman found previous procedures for carrying out the determination of aluminum by the aurin method to be unsatisfactory in that the colors of the solutions faded rapidly and were not well-reproducible. They have proposed a new procedure which is given below. These authors found that the rate of addition of ammonium hydroxide to the acidified sample solution containing aurin had a considerable effect on the results. It is hardly possible to add ammonia at such a constant speed that two solutions containing the same amount of aluminum will give identical colors. If two such solutions are reacidified with acetic acid, however, allowed to stand for 10–15 minutes and then neutralized again with ammonia added at a moderate rate, the same color intensities are obtained and no fading occurs on standing.

Beer's law is not followed by the colloidal suspension of the lake so that comparison must be made by the standard series method or a reference curve constructed.

A number of metals interfere, especially iron and beryllium which give red lakes also. The interference of these metals cannot be prevented and they must be removed. Certain elements will not interfere if ammonium carbonate is used with, or in place of, ammonium hydroxide in the procedure. These include the alkaline earth metals in moderate concentrations (10 mg. per 100 ml.), rare earths, zirconium (10 mg. per 100 ml.), thorium, and chromium. Magnesium in a concentration of 10 mg. per 100 ml. gives a pink color not discharged by ammonium carbonate, but in lower concentrations its effect can be prevented by the use of ammonium carbonate. Gallium in low concentrations (0.1 mg. per 100 ml.) gives no color, but at higher concentrations (2 mg. per 100 ml.) yields a red color even in the presence of ammonium carbonate. Indium and thallium in amounts up to 2 mg. or slightly more give no reaction. Quadrivalent vanadium alone (up to 2 mg. per 100 ml.) gives no color, but when as little as 0.1  $\gamma$  of aluminum is present a deep color develops followed by the formation of a precipitate, which however dissolves in the course of 15 minutes, leaving the solution the same color as a blank. Quinquevalent vanadium in small amounts (1 mg.) does not interfere, but larger quantities give a color.

Metals such as titanium, molybdenum, tungsten, zinc, cadmium, lead, germanium, arsenic, etc. are without effect, at least in small amounts.

Ruthenium yields a colored solution, platinum gives a yellow chloroplatinate, and gold is reduced to the metal.<sup>7</sup>

Nitric acid, sulfur dioxide, hydrogen sulfide, and fluoride bleach the

<sup>7</sup> G. E. F. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis*. Wiley, New York, 1938; p. 175.

color, but all these can be removed by evaporating to fumes with sulfuric acid. Phosphoric acid in large amounts reduces the color intensity but below 25 mg. in 100 ml. of solution has little effect.

#### Special Solutions

*Ammonium aurintricarboxylate*, 0.2 per cent aqueous solution prepared from a tested product.

*Hydrochloric acid* (for Procedure 1), 1:9 (ca. 1.2 *N*).

*Ammonium acetate* (for Procedure 1), 10 per cent.

*Ammonium hydroxide-ammonium carbonate* (for Procedure 2). Saturate concentrated ammonium hydroxide with ammonium carbonate at approximately 25°. This solution is preferably prepared fresh.

*Standard aluminum solution*, 0.010 mg. Al per ml. in 0.1 *N* hydrochloric or sulfuric acid. Prepare from uneffloresced potassium alum ( $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}/\text{Al} = 17.6$ ) or from pure metallic aluminum.

#### ¶ Procedure 1: Determination in Acid Medium

Transfer 5–10 ml. of very nearly neutral sample solution containing 1–25  $\gamma$  of aluminum to a 25 ml. volumetric flask. Add 1.00 ml. of 1:9 hydrochloric acid (the sample solution should not contain acetate or any other substance buffering the acid) and 1.00 ml. of ammonium aurintricarboxylate solution. Dilute to about 15 ml. and add 5.0 ml. of ammonium acetate solution. Make up to the mark with water and determine the transmittancy after 15 minutes with the aid of a green filter (ca. 520  $m\mu$ ).

#### ¶ Procedure 2: Determination in Basic Medium<sup>8</sup>

The following directions apply to a solution having a volume of 40 to 75 ml. and containing 0.01 to 0.1 mg. of aluminum. Iron, beryllium, etc. (see above) must be absent.

Add 5 ml. of concentrated hydrochloric acid, 5 ml. of glacial acetic acid, and 5 ml. of ammonium aurintricarboxylate solution. Next add ammonium hydroxide (or ammonium hydroxide-ammonium carbonate if alkaline earths, rare earths or other elements mentioned above are present) while stirring, until the cloudy appearance of the dye disappears and the solution becomes clear, but is still acid to litmus and strongly colored. Place a piece of litmus paper against the wall of the beaker, and while constantly stirring add ammonium hydroxide (or ammonium hydroxide-ammonium carbonate) at the rate of approximately 1 drop every 2 seconds until 2 ml. have been added; then add 1 drop every 3–4 seconds until the litmus paper becomes blue. Next add 5 ml. of glacial acetic acid, allow to stand for 10 minutes, and neutralize the solution as previously described. Finally add 5 ml. of ammonium hydroxide (or ammonium hydroxide-ammonium

<sup>8</sup> J. A. Scherrer and W. D. Mogeran, *J. Research Natl. Bur. Standards*, **21**, 105 (1938).

carbonate). Allow the solution to cool to room temperature and compare against standard solutions similarly treated.

### B. THE HEMATOXYLIN METHOD<sup>9</sup>

Hematoxylin gives a violet-purple lake with aluminum in slightly basic solution, the optimum pH range being 7-8.5. On acidification (pH ca. 4.5) the lake is stabilized and the color of the excess dye changes from red to yellow. Ferric iron under the same conditions yields a bluish lake and interferes seriously. The absorption curves of the aluminum and iron lakes overlap but the absorption maxima are sufficiently far apart to enable aluminum to be determined in the presence of a comparable amount of iron by measurement of the optical densities of the solution at wave lengths corresponding to the two absorption maxima.

The suspensions of both the aluminum and iron lakes follow Beer's law, so that the following equations hold:<sup>9</sup>

$$\text{Log} \left( \frac{I_0}{I} \right)_{\text{Al}}^A = K_{\text{Al}}^A C_{\text{Al}}$$

$$\text{Log} \left( \frac{I_0}{I} \right)_{\text{Fe}}^A = K_{\text{Fe}}^A C_{\text{Fe}}$$

where:  $I_0$  = intensity of light passing through the pure solvent,

$I$  = intensity of light passing through the colored solution of concentration  $C$ ,

$K$  = constant depending on wave length and thickness of layer of solution,

and superscript  $A$  refers to filter giving maximum transmission at one of the absorption maxima.

$$d_{\text{Al}}^A = K_{\text{Al}}^A C_{\text{Al}} \quad (1)$$

where  $d_{\text{Al}}^A$  = partial density due to aluminum at wave length  $A$ .

Similarly

$$d_{\text{Fe}}^A = K_{\text{Fe}}^A C_{\text{Fe}} \quad (2)$$

The total density at wave length  $A$ ,  $D^A$ , is:

$$D^A = d_{\text{Al}}^A + d_{\text{Fe}}^A = K_{\text{Al}}^A C_{\text{Al}} + K_{\text{Fe}}^A C_{\text{Fe}} \quad (3)$$

Similarly at wave length  $B$ :

$$D^B = d_{\text{Al}}^B + d_{\text{Fe}}^B = K_{\text{Al}}^B C_{\text{Al}} + K_{\text{Fe}}^B C_{\text{Fe}} \quad (4)$$

<sup>9</sup> H. W. Knudson, V. W. Meloche, and C. Juday, *Ind. Eng. Chem., Anal. Ed.*, **12**, 715 (1940); W. D. Hatfield, *Ind. Eng. Chem.*, **16**, 233 (1924); J. L. Steenkamp, *J. S. African Chem. Inst.*, **13**, 64 (1930).

From equations 3 and 4:

$$C_{Al} = \frac{K_{Fe}^A D^B - K_{Fe}^B D^A}{K_{Fe}^A K_{Al}^B - K_{Fe}^B K_{Al}^A} \quad (5)$$

A plot of  $\log \frac{I_0}{I}$  against concentration gives a straight line if Beer's law holds, as it does in this case. Therefore  $K$  is the slope of the line. The values of  $K_{Al}^A$ ,  $K_{Fe}^A$ ,  $K_{Al}^B$  and  $K_{Fe}^B$  are found by making calibration curves for the aluminum and iron for each filter and determining the slopes of the respective lines.

Filters with maximum transmission at 540 m $\mu$  (corresponding to the maximum in the aluminum absorption curve) and 660 m $\mu$  (corresponding to the iron maximum) are suitable for differential spectral separation of the two metal lakes. Transmission of light below 500 m $\mu$  must be avoided because absorption by the excess hematoxylin becomes appreciable at wave lengths shorter than this.

The effect of other metals on the determination of aluminum by this method has not been systematically investigated. It is known that calcium and magnesium are without appreciable effect, at least in low concentrations.

The color of the aluminum-hematoxylin solutions changes quite rapidly on standing and comparisons or measurements should be made immediately after developing the color.

### Reagents

*Acetic acid, 35 per cent.* Prepare by dilution of glacial acetic acid (99 per cent).

*Ammonium carbonate.* Dissolve 50 g. of ammonium carbonate monohydrate in 200 ml. of water. Prepare fresh each 3 days, and keep cool.

*Hematoxylin solution.* Dissolve 0.1 g. of C. P. hematoxylin in 100 ml. of hot water and dilute to 200 ml. The solution is stable for 2-3 weeks.

*Starch solution.* Dissolve 2 g. of soluble starch in 100 ml. of boiling water.

### ¶ Procedure

The combined content of aluminum and ferric iron should not exceed about 0.3 p.p.m., and the aluminum content should be at least 0.05 p.p.m.

To 50 ml. of neutral sample add 1 ml. of starch solution and 1.0 ml. of hematoxylin solution, mix, and then add 1.0 ml. of ammonium carbonate solution. Mix, allow the solution to stand for 10 minutes, and add 1 ml. of acetic acid so as to obtain a mixture having a pH of 4.5-4.6. Remove excess carbon dioxide by shaking. Transfer the solution to an absorption cell and immediately obtain the optical density of the solution using filters giving maximum transmission at 540 and 660 m $\mu$ . Substitute the values obtained in Equation 5 above, and solve for the aluminum concentration.



Obtain the values of the constants in Equation 5 by treating known solutions of aluminum and iron (containing from 0.1 to 0.3 p.p.m.) as described.

The above procedure may be used for the determination aluminum in water, the sample being concentrated if necessary so that at least 0.05 p.p.m. of Al is present.

### C. OTHER METHODS

#### 1. With Reagents Forming Lakes

- a. Eriochrome cyanin-R<sup>10</sup>
- b. Alizarin S (sodium alizarinsulfonate).<sup>11</sup> For a procedure see p. 126.
- c. Quinalizarin (1,2,5,8-tetrahydroxyanthraquinone)<sup>12</sup> and hydroxymethylantraquinone.<sup>13</sup>

#### 2. With 8-Hydroxyquinoline

The aluminum oxinate may be determined by conversion of the oxine in the precipitate into an azo dye.<sup>14</sup> Also, phosphomolybdotungstic acid may be reduced by the oxine in the precipitate.<sup>15</sup> See also p. 95.

#### 3. With Morin<sup>16</sup> and Quercetin<sup>17</sup>

Fluorescence methods.

#### 4. With Cupferron<sup>18</sup>

Nephelometric and turbidimetric.

<sup>10</sup> F. Alten, W. Weiland, and E. Knippenberg, *Z. anal. Chem.*, **96**, 91 (1934); F. Alten, B. Wandrowski, and E. Hille, *Angew. Chem.*, **48**, 273 (1935); T. Millner, *Z. anal. Chem.*, **113**, 83 (1938); T. Millner and F. Kunos, *ibid.*, **113**, 102 (1938).

<sup>11</sup> F. W. Atack, *J. Soc. Chem. Ind.*, **34**, 641, 936 (1915); D. S. Savchenko, *Zavodskaya Lab.*, **1933**, No. 2, p. 23; J. H. Yoe and W. L. Hill, *J. Am. Chem. Soc.*, **50**, 748 (1928); F. P. Underhill and F. I. Peterman, *Am. J. Physiol.*, **90**, 1 (1929); A. Stock, D. Praetorius, and O. Preiss, *Ber.*, **58**, 1571 (1925); J. Joshii and T. Jimbo, *Science Repts. Tôhoku Imp. Univ.*, **21**, 65 (1932); A. P. Musakin, *Z. anal. Chem.*, **105**, 351 (1936). Consult especially the paper of Musakin.

<sup>12</sup> I. M. Kolthoff, *Chem. Weekblad*, **24**, 447 (1927); *J. Am. Pharm. Assoc.*, **17**, 360 (1928).

<sup>13</sup> I. M. Kolthoff, *J. Am. Pharm. Assoc.*, **17**, 360 (1928).

<sup>14</sup> F. Alten, H. Weiland and H. Loofmann, *Angew. Chem.*, **46**, 668 (1933); O. Schams, *Mikrochemie*, **25**, 16 (1938).

<sup>15</sup> M. Teitelbaum, *Z. anal. Chem.*, **82**, 366 (1930).

<sup>16</sup> C. E. White and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.*, **12**, 229 (1940).

<sup>17</sup> A. L. Davydov and U. S. Devekki, *Zavodskaya Lab.*, **10**, 134 (1941).

<sup>18</sup> L. de Brouckère and E. Belcke, *Bull. soc. chim. Belg.*, **36**, 288 (1927).

## III. Applications

## A. NON-FERROUS ALLOYS

The following procedure<sup>19</sup> was worked out for the determination of aluminum in bearing metals, solders, etc. but it should have more general applicability. Most of the interfering metals are removed by electrolysis with a mercury cathode.

## ¶ Procedure

Dissolve a suitable weight of sample (0.01 to 0.10 mg. of Al) in an appropriate acid; sulfuric acid may often be used, but if another acid is required, convert the metals to sulfates by gentle fuming with sulfuric

TABLE 14

DETERMINATION OF ALUMINUM IN NON-FERROUS ALLOYS WITH ALUMINON AFTER REMOVAL OF INTERFERING ELEMENTS BY ELECTROLYSIS WITH A MERCURY CATHODE<sup>a</sup>

Material	Al added mg.	Al found mg.
Antifriction metal (63.7% Pb, 20.5% Sn, 14.0% Sb, 1.6% Cu), 1 g. sample	None	None
	.03	0.03
	0.05	0.05
	0.08	0.08
Bearing metal (79% Pb, 11% Sn, 10% Sb), 1.0 and 0.5 g. samples	None	<0.001
	0.10	0.10
Solder (50% Sb, 50% Sn), 1.0 g. sample	None	None
	0.05	0.05 <sup>b</sup>

<sup>a</sup> Figures from Scherrer and Mogerman.<sup>19</sup>

<sup>b</sup> Lead sulfate filtered off before electrolysis.

acid, taking care that no nitric or hydrochloric acid remains. Dilute the solution, containing a minimum of sulfuric acid (not more than 5 ml.), to approximately 25 ml. Filter off any lead sulfate and wash the filtrate into a modified Melaven cell<sup>20</sup> provided with a motor stirrer and containing about 50 ml. of mercury.<sup>21</sup> Electrolyze with the highest current that

<sup>19</sup> J. A. Scherrer and W. D. Mogerman, *J. Research Natl. Bur. Standards*, **21**, 107 (1938).

<sup>20</sup> *Ind. Eng. Chem., Anal. Ed.*, **2**, 180 (1930).

<sup>21</sup> The apparatus consists of a cylindrical electrolysis vessel (20 cm. in height and 3.5 cm. in diameter) provided at the bottom with a double-bored stopcock, one bore of which connects by means of rubber tubing with a similar slightly smaller vessel containing mercury; the other bore connects with a glass tube through which the solution is led off at the end of the electrolysis. The stirrer for the electrolysis vessel

will not cause boiling of the solution or excessive spraying (ordinarily 3 to 5 amperes). Stir the mercury and the solution vigorously during the electrolysis. One gram of copper or iron can usually be deposited in 35 to 45 minutes, and a like amount of tin, antimony, lead or zinc in 2 to 3 hours. Care should be taken to wash down any spray that collects on the walls of the cell.

When the electrolysis is complete, separate the mercury and the aqueous solution while keeping the current at least partially on. If loose particles of amalgam float in the solution remove them by filtration. Then determine aluminum in the solution according to one of the general procedures above, using the whole volume (40-75 ml.) or an aliquot.

### B. BIOLOGICAL MATERIALS

The following directions for the isolation of aluminum are those of Cholak, Hubbard and Story.<sup>22</sup> These authors use alizarin S for the determination of aluminum.

#### ¶ Procedure

Take a suitable weight of sample (5 g. or less of blood, 5 to 50 g. of tissue, 100 ml. or less of urine) and destroy organic matter by acid oxidation (*cf.* p. 278) or by ashing. In the latter procedure use a platinum dish and ignite in a muffle furnace at about 500° C. until all or nearly all of the carbonaceous material has been destroyed. Treat the ash with 5 ml. (or more if judged necessary) of concentrated hydrochloric acid and 10 ml. of water, and evaporate just to dryness. Add 10 to 20 ml. of 1:5 hydrochloric acid, keep near the boiling point for 10 minutes, centrifuge or filter through a very small quantitative paper which has been washed with dilute hydrochloric acid, and wash the residue with a little dilute hydrochloric acid. Transfer the residue or the paper to a platinum crucible, ignite if necessary, and add a little sulfuric and hydrofluoric acid. Evaporate to dryness, add a few drops of dilute sulfuric acid, and evaporate to fumes to expel all hydrofluoric acid. Add a milliliter or two of dilute hydrochloric acid and warm. A clear solution should be obtained; combine it with the main solution.

Add 1 mg. of iron as any ferric salt<sup>23</sup> to the solution of the decomposed

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has two propellers, one dipping into the mercury and the other into the aqueous solution. A platinum wire 0.1 cm. in diameter serves as anode; it is dipped about 12 cm. into the solution. For a description of a larger electrolysis cell see M. H. Steinmetz, *Ind. Eng. Chem., Anal. Ed.*, **14**, 109 (1942).

<sup>22</sup> J. Cholak, D. M. Hubbard, and R. V. Story, *Ind. Eng. Chem., Anal. Ed.*, **15**, 57 (1943).

<sup>23</sup> If the sample contains sufficient iron, as is the case with blood, omit this addition; similarly if the sample contains much phosphate an additional amount of this need not be added.

sample (volume of about 25 ml.) together with 1 ml. of saturated ammonium acetate and 200 mg. of diammonium phosphate. Then add 5 drops of 0.1 per cent aqueous bromocresol green indicator solution. Next add ammonium hydroxide until the *pH* of the solution is 4.2 (compare against a buffer). Heat on the steam bath for one-half hour and collect the precipitate by filtration (use a porous porcelain or sintered glass filter crucible) or by centrifuging. Wash the ferric-aluminum phosphate precipitate with small portions of warm water.

Dissolve the phosphate precipitate in 5 ml. of warm 1:10 sulfuric acid and dilute to 10 ml. with water. If the liquid contains any separated silica remove the latter by centrifuging or filtering. Transfer the clear solution to a separatory funnel and dilute to 20–25 ml. Add 2 ml. of freshly prepared 6 per cent aqueous cupferron solution. Mix and allow to stand for a few minutes. Add 10 ml. of a 1:1 volume mixture of benzene-ethyl ether (saturated with water), shake for a minute, and allow the phases to separate. Draw off the aqueous layer and extract again with a 10 ml. portion of benzene-ether. Transfer the aqueous solution to a 30 ml. Kjeldahl flask or a small Erlenmeyer flask, add 1 ml. of concentrated nitric acid, and heat until fumes of sulfuric acid appear. Cool, add a milliliter of water, and again heat to fumes of sulfuric acid. Dilute the residual acid with water, transfer to a 25 ml. volumetric flask and dilute to the mark. Take a 10 ml. aliquot (1 to 25  $\gamma$  of aluminum), neutralize with ammonia, and determine aluminum by the aurintricarboxylate method according to Procedure 1, p. 120.

Alternatively, aluminum can be determined with alizarin S as follows. For the 0–5  $\gamma$  aluminum range dilute the residue from the destruction of excess cupferron to 14 ml. in a glass-stoppered cylinder, add 1 ml. of a 0.075 per cent aqueous solution of alizarin red S and 10 ml. of 3:7 ammonium hydroxide, mix, and determine the transmittancy immediately at 580  $m\mu$ . For the range 0–50  $\gamma$  aluminum, dilute to 85 ml., and add 5 ml. of alizarin red S and 10 ml. of dilute ammonia. Beer's law is obeyed.

It is important to run a blank determination through the whole procedure.

## CHAPTER VI

### ANTIMONY

The determination of minute amounts of antimony is not often required, and fortunately so, because the trace chemistry of this element is not well developed.

#### I. Separations

The precipitability of antimony sulfide (III or V) in dilute mineral acid solutions (1 *N* or less in hydrochloric acid) will at times be of value in separating minute quantities of antimony. Possibly precipitation in the presence of oxalate (separation from quadrivalent tin) or fluoride (separation from tin and germanium) may find application in trace analysis as well as in macro analysis. Whether relatively much arsenic (III) can be separated from very little antimony (III) by sulfide precipitation in strong hydrochloric acid (6–9 *N*) is not known; loss of antimony by coprecipitation or postprecipitation is to be feared. The solubility of antimony sulfide in basic solution finds application at times in separations, as from copper (p. 134).

Antimony trichloride can be volatilized from a sulfuric acid solution at a temperature of 200° C. in the presence of a reducing agent such as sulfur by leading a stream of hydrogen chloride through the mixture. Volatilization as the bromide can be carried out more easily (see p. 31). Arsenious chloride is volatilized at a much lower temperature (105°) than antimony chloride and the possibility exists that relatively much arsenic can be separated from little antimony by fractional distillation or volatilization.<sup>1</sup>

Evolution of antimony as stibine has been employed for the isolation of traces of the element, but the method has not been fully exploited as yet. Conversion of antimony to stibine may be effected by the action of zinc in hydrochloric acid solution<sup>2</sup> or by electrolysis of a hydrochloric acid solution with a lead cathode, over which a stream of hydrogen is passed.<sup>3</sup> The stibine may be decomposed by passage through a heated glass tube and antimony deposited. It should also be possible to absorb the stibine in a silver nitrate or mercuric chloride solution.

<sup>1</sup> Cf. H. Biltz and W. Biltz, *Ausführung quantitativer Analysen*. Hirzel, Leipzig, 1930; p. 327. See especially J. A. Scherrer, *J. Research Natl. Bur. Standards*, **16**, 253 (1936); **21**, 95 (1938).

<sup>2</sup> C. R. Sanger and J. A. Gibson, *J. Soc. Chem. Ind.*, **26**, 58 (1907).

<sup>3</sup> J. Grant, *Analyst*, **53**, 626 (1928); H. J. S. Sand, *Electrochemistry and Electrochemical Analysis*, Vol. II. Chemical Publ. Co., Brooklyn, 1940; p. 141.

Antimony can be plated out on copper in a hydrochloric acid solution (the Reinsch reaction). Prior separation of arsenic can be effected by precipitation with hypophosphite. Details are given on p. 134. Antimony can also be deposited by internal electrolysis from a hot dilute hydrochloric acid solution containing hydrazine hydrochloride; a spiral of copper wire is used as cathode, and iron or lead as the anode.<sup>4</sup> The electrolysis proceeds slowly unless about 1 mg. of arsenic is added.

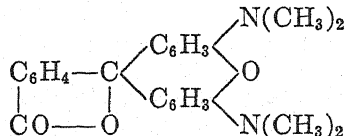
In weakly acid solution, antimony can be coprecipitated with manganese dioxide (obtained by adding permanganate to a solution containing manganoous salt).<sup>5</sup> Much copper does not interfere. Ferric hydroxide is also a good collector for antimony (separation from copper and molybdenum).

Small amounts of many heavy metals (silver, mercury, copper, bismuth, nickel, cadmium, zinc, etc.) can be separated from antimony by extraction with dithizone from a weakly ammoniacal solution containing tartrate or citrate. Arsenic remains with the antimony.

## II. Methods of Determination

### A. THE RHODAMINE B METHOD

In hydrochloric acid or in sulfuric acid solution containing chloride, quinquevalent antimony reacts with rhodamine B (tetraethylrhodamine)



to give an insoluble red compound of unknown composition. After destruction of the excess reagent with bromine, this compound may be dissolved in alcohol and determined colorimetrically.<sup>6</sup> A great many cations and anions interfere. The method can not be considered ideal, but it affords useful results when the amount of antimony is in the vicinity of 50  $\gamma$ . The directions of Fredrick follow.

#### Special Solutions

*Sulfuric acid*, 25 per cent. 125 ml. of concentrated acid diluted to 500 ml. with water.

*Ceric sulfate*, 0.1 *N* in 1 *N* sulfuric acid (3.3 g. of anhydrous ceric sulfate in 100 ml.).

*Sodium thiosulfate*, 0.1 *N* (2.5 g. of pentahydrate in 100 ml. of water).

*Lithium chloride*, 25 g. in 100 ml. of aqueous solution.

<sup>4</sup> Y. Y. Lur'e, E. M. Tal and L. B. Fligel'man, *Zavodskaya Lab.*, **8**, 1222 (1939).

<sup>5</sup> B. Park and E. J. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **5**, 182 (1933); C. L. Luke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 626 (1943). Cf. the references given under bismuth on p. 158.

<sup>6</sup> W. G. Fredrick, *Ind. Eng. Chem., Anal. Ed.*, **13**, 922 (1941).

*Bromine water*, saturated.

*Rhodamine B*, 0.2 per cent aqueous solution (filtered if necessary).

*Hydroxylamine hydrochloride*, 1 per cent aqueous solution.

*Standard antimony solution*, 0.010 per cent. Dissolve 0.100 g. of pure antimony in 25 ml. of hot concentrated sulfuric acid, cool, make up to 100 ml. with water, and dilute 10 ml. of this solution together with 25 ml. of concentrated sulfuric acid to 100 ml. with water. The standard solution may also be prepared from potassium antimonyl tartrate (p. 131).

## ¶ Procedure

Transfer 1–5 ml. of sample solution in 25 per cent (9 *N*) sulfuric acid, containing 50–250  $\gamma$  of antimony, to a glass-stoppered 50 ml. graduated cylinder. Dilute to 5 ml. with 25 per cent sulfuric acid, added so as to rinse down the walls. Add successively, with mixing, 1 ml. of lithium chloride, 0.1 ml. of ceric sulfate (or enough to give a faint yellow color), and sufficient hydroxylamine hydrochloride solution to destroy the yellow color. Cool in an ice bath for 15 minutes, add 1 ml. of rhodamine solution (1.5 ml. for 150  $\gamma$  Sb and 2.0 ml. for 200–300  $\gamma$  Sb), and cool further for 10 minutes. Add 10 ml. of water and again cool in the ice bath for 10 minutes. Now add 0.10 ml. of bromine water, mix quickly, immediately add 0.10 ml. of sodium thiosulfate solution, and swirl. (These solutions should be added directly to the sample solution, and not down the side of the cylinder.) Add 20 ml. of ethyl alcohol (95 per cent) at once, mix, and dilute to 50 ml. with water. After 20 or 30 minutes compare against a similar standard prepared in the same manner. If a photometer is used, determine the extinction at 525  $m\mu$ .

For less than 25  $\gamma$  of antimony the standard series method should be used instead of the balancing method with a Duboscq colorimeter. In this case use 0.5 ml. of rhodamine B.

A blank must be run.

**Notes.**—1. The destruction of the excess rhodamine B is the crucial step in the procedure. The amount of bromine added must not be too great and the excess must be destroyed promptly. The temperature must be kept below 10° C.

2. A blank shows a faint residual color, whose intensity increases with the amount of rhodamine B added.

3. The acidity of the solution affects both the color of the solution of the antimony complex and the bleaching of the excess reagent by bromine, and it should not vary by more than 5 per cent from that specified.

4. The color intensity is influenced by the temperature, but does not change appreciably with time.

5. Beer's law is obeyed by the alcoholic solution of the complex.

6. Lithium chloride is the only suitable chloride soluble in the alcoholic solution.

7. 1:1 Hydrochloric acid may be used in place of 25 per cent sulfuric acid but the latter is preferable.

8. For quantities of antimony below 10  $\gamma$ , errors as great as 25 per cent may be encountered. For larger amounts (100  $\gamma$ ) the error will usually not exceed 5 per cent.

## B. THE PYRIDINE-IODIDE METHOD

Various organic bases form slightly soluble colored double iodides with trivalent antimony (quintivalent antimony gives the same reactions since it is reduced to the trivalent form by iodide) of the general formula  $B \cdot HI \cdot SbI_3$ . Clarke<sup>7</sup> has worked out a method based on the formation of yellow pyridine antimony iodide, kept in suspension by gum arabic. The solution is acidified with sulfuric acid. Chloride ion decreases the color intensity or destroys the color entirely. The maximum color intensity is

TABLE 15  
INTERFERENCES IN THE RHODAMINE B METHOD ACCORDING TO FREDRICK<sup>6</sup>  
(100  $\gamma$  Sb in each case.)

Substance	Amount mg.	Effect
Al	7.5	None
Bi	7.5	None
Mg	7.5	None
Mn	7.5	None
H <sub>2</sub> PO <sub>4</sub>	200	None
As <sup>III</sup> , As <sup>V</sup>	Trace <sup>a</sup>	Hue changed
Ce	1.0 <sup>a</sup>	Hue changed
Fe	4.0 <sup>a</sup>	Hue changed
Tl	Trace <sup>a</sup>	Hue changed
NaF	1 <sup>a</sup>	Hue changed
NaNO <sub>3</sub>	1 <sup>a</sup>	Hue changed
Cd	3.0 <sup>a</sup>	Color intensity increased
Hg	0.5 <sup>a</sup>	Color intensity increased
Sn	3.5 <sup>a</sup>	Color intensity increased
Zn	3.5 <sup>a</sup>	Color intensity increased
HClO <sub>4</sub>	Trace <sup>a</sup>	Color intensity increased
Cu	Trace <sup>a</sup>	Color intensity decreased
Ni	7.5 <sup>a</sup>	Color intensity decreased
NaNO <sub>2</sub>	Trace <sup>a</sup>	Color intensity decreased
NaBr	0.5 <sup>a</sup>	Color intensity decreased

<sup>a</sup> Maximum permissible amount (100  $\gamma$  Sb).

attained in a solution which is 6 to 8 *N* in sulfuric acid. The iodide concentration should correspond to 1 per cent potassium iodide in the final solution. Too much pyridine bleaches the color. Alkali sulfates have no appreciable effect. The liberation of iodine by atmospheric oxidation is prevented by the addition of a small amount of sulfurous acid. The concentration of the latter must be kept low, else a yellow color is produced (see p. 161).

<sup>7</sup> S. G. Clarke, *Analyst*, **53**, 373 (1928).



Tin and arsenic in low concentrations (several centigrams in 100 ml.) give no color and do not interfere with the determination. A number of heavy metals give slightly soluble iodides or double iodides, or liberate iodine. Bismuth gives an orange precipitate, nickel a green, cobalt a pink, zinc a white precipitate, etc.

#### Special Solutions

*Pyridine*, 10 per cent aqueous solution.

*Potassium iodide*, 20 per cent aqueous solution, freshly prepared.

*Gum arabic*, 1 per cent in water.

*Sulfur dioxide*. Saturate cold water with sulfur dioxide and dilute with 9 times its volume of water. Prepare fresh.

*Standard antimony solution*, 0.100 mg. Sb per ml. Dissolve 0.0274 g. of potassium antimonyl tartrate in 60 ml. of 6 *N* sulfuric acid and dilute to 100 ml. with water.

#### ¶ Procedure

Into a flat-bottomed tube of 25–30 ml. capacity measure 1 ml. of gum arabic solution, 0.5 ml. of potassium iodide, 0.10 ml. of pyridine solution, 0.10 ml. of sulfur dioxide solution, and 6 ml. of 1:3 sulfuric acid. To this mixture add a 1:3 sulfuric acid solution of the sample<sup>8</sup> having a volume of 3–4 ml. and containing not more than 0.1 mg. of antimony. The comparison mixture should contain the same amounts of iodide, pyridine, etc. as the unknown solution, but 9 to 10 ml. of 1:3 sulfuric acid instead of the 6 ml. in the sample tube. From a microburet add the standard antimony solution with shaking or stirring until the colors match when the tubes are viewed axially. Adjust the volumes near the end point by the addition of water so that they are approximately the same.

If the color intensity is very low, the double iodide may be extracted with a small volume of amyl alcohol.<sup>9</sup>

#### C. THE IODIDE METHOD<sup>10</sup>

In an acid solution, iodide in excess yields iodoantimonite ion with antimony (quinquevalent antimony is reduced to the trivalent state and iodine is liberated) which has a strong yellow color. In a concentrated solution of potassium iodide the sensitivity approaches that of the bismuth-iodide reaction, but since the liberation of iodine by air-oxidation is difficult to prevent in strong iodide solution, one must generally restrict the amount of iodide used. Nevertheless under the conditions described below as little as 2  $\gamma$  of antimony will produce a faint color when a tube 1.5 cm. in diameter is used to hold the solution. The liberation of iodine by air-oxidation

<sup>8</sup> The solution should contain no chloride. Chloride may be removed by evaporating to fumes of sulfuric acid after adding nitric acid to prevent loss of antimony.

<sup>9</sup> A. A. Vasil'ev and M. E. Shub, *J. Applied Chem. U. S. S. R.*, **6**, 560 (1933).

<sup>10</sup> Cf. L. Fauchon, *J. pharm. chim.*, **25**, 537 (1937).

can be prevented by adding hypophosphite to the acid solution. The reaction between iodine and hypophosphite under the conditions of the determination is so slow that the liberation of more than traces of iodine by the action of oxidizing substances must not be allowed to occur. Stannous chloride is a better reagent than sodium hypophosphite for the destruction of iodine but unfortunately in strong iodide solutions tin yields a yellow color.

Bismuth must naturally be absent. Small amounts of lead, mercury, arsenic (0.1–0.2 mg.  $\text{As}^{\text{III}}$ ), and copper may be present; the iodine liberated by cupric copper reacts fairly rapidly with hypophosphite, copper apparently exercising a catalytic effect.

#### Reagent

*Potassium iodide-sodium hypophosphite.* Dissolve 100 g. of potassium iodide and 10 g. of sodium hypophosphite in 100 ml. of water.<sup>11</sup>

#### ¶ Procedure

To 5 ml. of a sulfuric acid solution (1 *N*) of antimony (III) add 2.0 ml. of potassium iodide-hypophosphite reagent, mix, and after 5 minutes or more compare against a series of similar standards. Care must be taken to have the iodide concentration the same in all the solutions since the color intensity is greatly dependent upon it. A blank should be included in the series to assure prevention of error from any unreduced iodine in the reagent.

#### D. THE SULFIDE METHOD

This unspecific method is fairly sensitive, so that it is occasionally valuable when other metals yielding sulfides insoluble in mineral acids are absent. It may for instance be applied after evolving antimony as stibine, decomposing the latter by passage through a heated tube, and dissolving the deposit of antimony in strong hydrochloric acid. It is said that arsenic does not interfere because it is not appreciably dissolved by hydrochloric acid.<sup>12</sup>

#### ¶ Procedure

Make the antimony (III) solution 2 *N* in hydrochloric acid, add 2 ml. of clear saturated hydrogen sulfide water for each 10 ml. of sample (containing from 2 to 20  $\gamma$  or slightly more of antimony), and compare against standards similarly treated. As long as the antimony concentration is

<sup>11</sup> On standing the solution slowly becomes yellow. A slight yellow color does no harm because when the reagent is added to the acidified sample solution the iodine is reduced. Since the reaction between iodine and hypophosphite is slow, however, the reagent should be discarded if it acquires a pronounced yellow color.

<sup>12</sup> J. Grant, *Analyst*, **53**, 626 (1928).

less than 2 or 3  $\gamma$  per ml. the addition of a protective colloid such as gum arabic is unnecessary. If the addition of gum arabic seems desirable, add 0.1 ml. of 5 per cent solution to 10 ml. of sample.

#### E. THE STIBINE METHOD

A method for the determination of antimony in spray residues has been described in which stibine is evolved by the action of zinc in hydrochloric acid solution and led over a strip of paper impregnated with mercuric chloride as in the Gutzeit method for arsenic.<sup>13</sup> The length of the stain is measured after immersion of the paper in 5 per cent ammonia solution. The method is suitable for 25 to 150  $\gamma$  of antimony. Arsenic interferes. Organic material may be ashed at 550° C. without loss of antimony originally present as potassium antimonyl tartrate.

#### F. THE PHOSPHOMOLYBDOTUNGSTIC ACID METHOD<sup>14</sup>

Trivalent antimony reduces phosphomolybdotungstic acid in dilute acid solutions with the production of a blue color. As little as 0.05 mg. of antimony in 100 ml. can be determined in this way. Sulfur dioxide is suitable for the reduction of antimony to the trivalent state. This method has been applied to the determination of antimony in copper, after isolation of antimony by coprecipitation with manganese dioxide produced by addition of permanganate to a boiling solution containing manganous sulfate; it is stated that silver, ferrous iron, nickel, cobalt, arsenic, and bismuth do not interfere.

#### ¶ Procedure

Add aqueous sulfur dioxide solution or a little solid sodium sulfite to the 3 *N* hydrochloric acid solution of the sample, and boil to expel all excess sulfur dioxide. Cool and adjust the acidity to 0.02–0.1 *N* ( $\beta$ -dinitrophenol is a suitable indicator). Add dropwise a solution of Folin's reagent (p. 412), whose acidity has been reduced to 0.1 *N*, until a color appears, heat the solution to develop the full color, and compare against a standard which has been treated in the same way.

### III. Special Applications

#### A. DETERMINATION OF TRACES OF ANTIMONY IN COPPER AND COPPER ALLOYS<sup>15</sup>

The procedure involves reduction of cupric copper in acid solution by sodium hypophosphite, deposition of antimony on metallic copper, stripping

<sup>13</sup> J. Davidson, G. N. Pulley, and C. C. Cassil, *J. Assoc. Official Agr. Chem.*, **21**, 314 (1938).

<sup>14</sup> S. Makishima, *J. Soc. Chem. Ind. Japan*, **34**, Suppl. binding, 322 (1931).

<sup>15</sup> S. G. Clarke and B. S. Evans, *Analyst*, **54**, 23 (1929).

the antimony film with sodium peroxide, and determination of antimony by the pyridine-iodide method.

### ¶ Procedure

Dissolve 5 g. of sample (copper, bronze, cupro-nickel, brass, etc.) in 30 ml. of 1:3 sulfuric acid and 15 ml. of concentrated nitric acid; evaporate until the sulfuric acid fumes strongly. Cool, dissolve the residue in 150 ml. of water, and add 150 ml. of concentrated hydrochloric acid and 10 g. of sodium hypophosphite. Boil for 10 minutes. If appreciable amounts of arsenic are absent proceed immediately as directed in the next paragraph. If a brown-black precipitate of arsenic separates, however, boil further for 20 minutes, cool, and shake the liquid with 20 ml. of benzene to coagulate the precipitate. Filter through a moist filter paper and wash with a minimum amount of hot water; reject the precipitate. In the case of tin bronze, dissolve 10 g. of oxalic acid in the hydrochloric acid solution before the addition of hypophosphite; ignore any white turbidity produced.

Roll a piece of pure electrolytic copper foil,  $2.5 \times 20$  cm., into a flat spiral, clean by warming gently with dilute nitric acid (sp. gr. 1.2), wash with water, and drop it into the solution contained in a flask. Boil the solution gently for 2 hours, preferably with the coil upright, not on its side, in the liquid. Then lift the coil out of the solution with a hooked glass rod, rinse quickly by plunging into a beaker of water, and place without delay in a small beaker having a diameter only slightly greater than that of the coil. Cover with distilled water and add 1 g. of sodium peroxide at once. After allowing the solution to stand for 5-10 minutes, warm gently so that the copper becomes darkened with a layer of oxide. Pour off the liquid into a small flask, and rinse the coil twice with water. Test for completeness of stripping of antimony by immersing the coil in dilute sulfuric acid, which will dissolve the copper oxide and allow any remaining antimony to be seen.

Treat the antimony solution with a rapid stream of hydrogen sulfide for 15 seconds and allow the mixture to stand on the water bath for one-half hour. Filter off the copper and bismuth sulfides on a small filter and wash lightly with 1 per cent ammonium nitrate solution. Add 5 ml. of concentrated sulfuric acid to the filtrate and evaporate to fumes, adding a few drops of nitric acid near the end. Take up the sulfuric acid solution with 15 ml. of water, heat just to the boiling point and cool. Filter the solution, if necessary, and determine antimony by the pyridine-iodide method described above, increasing the volume of the reagents proportionately. Preferably the amount of antimony should not exceed 0.5 mg. when 100 ml. Nessler tubes are used.

B. DETERMINATION OF SMALL AMOUNTS OF ANTIMONY IN MERCURY ORES<sup>16</sup>

## ¶ Procedure

The following procedure may be applied to mercury ores containing iron, arsenic, and silica.

Heat 1 to 2 g. of finely divided sample with 10–20 ml. of concentrated sulfuric acid in a Kjeldahl flask until the liquid becomes clear. Transfer the solution to a 250 ml. volumetric flask, make up to volume with 10 per cent sulfuric acid containing 1 per cent tartaric acid, and filter. Transfer to a Nessler tube, 10 ml. of 0.5 per cent gelatin solution, 5 ml. of 10 per cent potassium iodide solution, 1 ml. of 10 per cent pyridine solution, 1 ml. of 1:3 sulfurous acid, 60 ml. of 1:3 sulfuric acid, and 10 or 20 ml. of the sample solution. In a second Nessler tube prepare a comparison solution having the same composition as the one in the first tube, and add standard antimony solution (0.1 mg. Sb per ml.) until the colors match.

<sup>16</sup> M. Y. Shapiro, *Zavodskaya Lab.*, **8**, 986 (1939).

## CHAPTER VII

### ARSENIC

Thanks to the ease of separation of arsenic from other elements, and the precision and great sensitivity of the molybdenum blue method, minute amounts of arsenic can be determined colorimetrically without difficulty, provided there is no loss of the element in the decomposition of the sample. Until recent years small quantities of arsenic were determined nearly exclusively by the Gutzeit method, but now the position of the latter is seriously threatened by the rival molybdenum blue method, which, it seems likely, will displace the Gutzeit procedure.

#### I. Separations

A number of good direct methods for the separation of arsenic are available. The most generally applicable method involves distillation of arsenious chloride from hydrochloric acid solution. A reducing agent such as hydrazine sulfate, cuprous chloride, or ferrous sulfate is used to reduce quinquivalent arsenic to the trivalent form. The presence of bromide aids the reduction. Nitric acid and other strong oxidizing agents must be absent. The presence of sulfuric acid does no harm. Germanium accompanies arsenic in the distillation, and antimony may partially distil if the temperature rises above  $107^{\circ}$ . Neither of these elements interferes in the subsequent colorimetric determination. If phosphate is present in large amounts, the distillate should be redistilled under the same conditions as in the first distillation to avoid error due to any phosphorus carried over mechanically in the first distillation. Passage of carbon dioxide or nitrogen through the solution during the distillation facilitates the volatilization of arsenic. The distillate may be collected in cold water. Directions for carrying out the distillation with hydrazine sulfate as the reducing agent are given on p. 140.

The second important method of isolation involves volatilization of arsenic as arsine by the action of zinc in hydrochloric or sulfuric acid solution. This method may be applied to solutions not containing large amounts of reducible heavy metals which would be likely to interfere with the evolution of arsine; moderate amounts of iron may be present. The evolution method is conveniently used for solutions of decomposed organic material, silicates and other organic materials in which heavy metals, with the exception of iron, are not present in appreciable amounts. The evolved arsine may be decomposed into elemental arsenic by passage through a silica tube

heated to 800° C.,<sup>1</sup> or more conveniently it may be absorbed in an acid solution of mercuric chloride containing potassium permanganate,<sup>2</sup> in sodium hypobromite solution<sup>3</sup> or in a sodium bicarbonate solution of iodine. The chief source of error in the procedure is likely to be incomplete absorption of arsine. This method of separation can be carried out more rapidly and more conveniently than the arsenious chloride distillation method.

Trivalent arsenic can be extracted as the xanthate by carbon tetrachloride from acid solution.<sup>4</sup> Antimony and other metal xanthates which are also extracted may be removed from the carbon tetrachloride by washing with concentrated hydrochloric acid containing stannous chloride; this treatment does not affect arsenic (III) xanthate. The carbon tetrachloride may then be evaporated, the arsenic oxidized to the quinquevalent state with bromine, and determined by the molybdenum blue method. It is stated that aluminum, manganese, zinc, lead, mercury, cadmium, and bismuth do not interfere. A detailed procedure is not given here because there are no data to show how well microgram quantities of arsenic can be isolated in this way. Amounts of arsenic equal to, or greater than, 0.1 mg. show excellent recoveries.

Precipitation methods for the isolation of arsenic are of subordinate importance, for in most cases the methods mentioned above can be applied more expeditiously. Occasionally, precipitation of elemental arsenic by such reducing agents as stannous chloride, hypophosphite, and copper in acid solution may find application. Arsenic in the quinquevalent state can be coprecipitated with ferric hydroxide or magnesium ammonium phosphate.

## II. Methods of Determination

### A. THE MOLYBDENUM BLUE METHOD

In this method the isolated arsenic is brought into the quinquevalent state and ammonium molybdate is added to form a heteropoly molybdiarsenate which is then reduced by a suitable reducing agent to strongly colored "molybdenum blue", in which molybdenum is present in a lower valence, but whose constitution is uncertain. The conditions of reduction must be such that the molybdenum in the complex, but not the excess

<sup>1</sup> H. J. Morris and H. O. Calvery, *Ind. Eng. Chem., Anal. Ed.*, **9**, 447 (1937).

<sup>2</sup> E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **14**, 82 (1942). C. C. Cassil and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **22**, 436 (1939), used mercuric chloride solution alone for the absorption of arsine in a microvolumetric method for arsenic based on iodometric titration.

<sup>3</sup> M. B. Jacobs and J. Nagler, *Ind. Eng. Chem., Anal. Ed.*, **14**, 442 (1942).

<sup>4</sup> A. K. Klein and F. A. Vorhes, *J. Assoc. Official Agr. Chem.*, **22**, 121 (1939).

ammonium molybdate, which is more difficultly reducible, is attacked. Phosphate reacts in the same manner as arsenate and must be absent.

Stannous chloride<sup>5</sup> and a reduced molybdate reagent<sup>6</sup> have frequently been used as reductants, but hydrazine sulfate is generally preferable.<sup>7</sup> With the latter a stable blue color is obtained which shows no appreciable change in 24 hours. Heating is necessary to develop the color with hydrazine sulfate, but the time of heating has no effect on the color intensity as long as it is sufficient to give the maximum color. The acid concentration of the solution must be controlled. If the acidity is too low silicate will give a blue color, and if it is too high the color due to arsenic is decreased

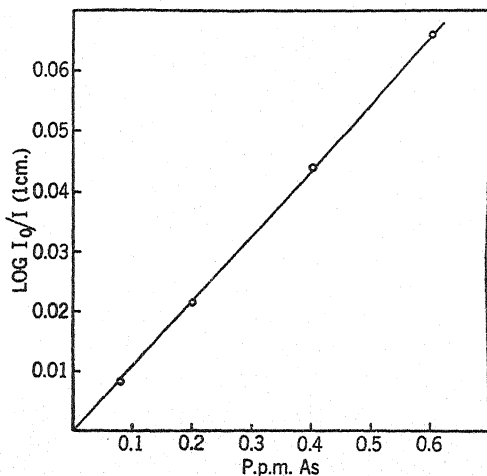


Fig. 22.—Determination of arsenic by the molybdenum blue method (red filter).

in intensity. The approximate optimum concentrations of sulfuric acid and ammonium molybdate in the final solution are stated to be 0.25 *N* and 0.05 per cent respectively.<sup>8</sup>

Two molybdenum blue procedures for the determination of arsenic are

<sup>5</sup> See for example G. Denigès, *Compt. rend.*, **171**, 802 (1920); E. Truog and A. H. Meyer, *Ind. Eng. Chem., Anal. Ed.*, **1**, 136 (1929).

<sup>6</sup> C. Zinzadze, *Ind. Eng. Chem., Anal. Ed.*, **7**, 230 (1935); J. T. Woods and M. G. Mellon, *ibid.*, **13**, 760 (1941).

<sup>7</sup> H. J. Morris and H. O. Calvery, *Ind. Eng. Chem., Anal. Ed.*, **9**, 447 (1937); E. H. Maechling and F. B. Flinn, *J. Lab. Clin. Med.*, **15**, 779 (1930).

<sup>8</sup> A. L. Chaney and H. J. Magnuson, *Ind. Eng. Chem., Anal. Ed.*, **12**, 693 (1940). In the procedure of C. J. Rodden, *J. Research Natl. Bur. Standards*, **24**, 7 (1940), the acid concentration is 0.5 *N* in sulfuric acid and the ammonium molybdate concentration is 0.1 per cent. These are the conditions originally prescribed by Morris and Calvery.<sup>7</sup>



given below, one for use after distillation of arsenious chloride, the other after evolution as arsine. Hydrazine sulfate is used as reducing agent in both procedures, but the composition of the molybdate-hydrazine sulfate reagent is different in the two cases. In the first procedure the arsenious chloride distillate is treated with nitric acid and evaporated to dryness to oxidize arsenic to the quinquevalent state and remove the excess acid.<sup>9</sup>

TABLE 16  
DETERMINATION OF ARSENIC IN ALLOYS BY THE MOLYBDENUM BLUE METHOD  
AFTER DISTILLATION AS THE CHLORIDE<sup>a</sup>

Arsenic present %	Arsenic found %	Sample
0.009	{ 0.008 0.009 0.009	Steel
0.024	{ 0.024 0.025	Ferromanganese
0.071	{ 0.068 0.070 0.071	Cast iron
0.19	{ 0.17 0.18	Phosphor-bronze bearing metal

<sup>a</sup> Figures from results reported by Rodden.<sup>11</sup>

TABLE 17  
DETERMINATION OF ARSENIC BY THE MOLYBDENUM BLUE METHOD  
AFTER EVOLUTION AS ARSINE

Arsenic taken, γ...	1.0	1.0	2.0	2.0	5.0	5.0	10.0	15.0	10.0 <sup>a</sup>	10.0 <sup>b</sup>
Arsenic found, γ...	0.9	0.9	1.8	2.0	4.8	5.2	9.8	15.1	9.5	9.8

<sup>a</sup> In the presence of 10 γ Sb.

<sup>b</sup> In the presence of 60 mg. Fe.

In the second procedure the mercuric chloride-potassium permanganate solution which is used to absorb and oxidize the arsine to arsenic acid may be treated directly with the molybdate-hydrazine sulfate reagent to develop the blue color; a small amount of mercurous chloride which is formed by

<sup>9</sup> Attention is called to a shorter procedure described by Chaney and Magnuson.<sup>8</sup> By using a still of special design, these authors are able to make the distillation in 5 minutes and keep the volume of the distillate small. Trivalent arsenic is oxidized with iodate instead of by evaporation with nitric acid.

reduction may be removed by rapid filtration.<sup>10</sup> Beer's law is followed in both procedures. As already mentioned, Method 1 is the most generally applicable, whereas Method 2 is restricted to samples not containing such heavy metals as lead and mercury, which prevent the complete liberation of arsine.

The accuracy of the methods may be judged from the figures given in Tables 16 and 17.

### *Method 1: Determination of Arsenic after Distillation of Arsenious Chloride<sup>11</sup>*

#### Apparatus

The distillation of arsenic trichloride should be made from an all-glass distilling apparatus such as that of Scherrer<sup>12</sup> shown in Fig. 23.

#### Special Solutions

*Hydrazine sulfate-ammonium molybdate.* Dissolve (a) 1 g. of ammonium molybdate in 100 ml. of 5 N sulfuric acid, and (b) 0.15 g. of hydrazine sulfate in 100 ml. of water. Dilute 10 ml. of solution (a) to 90 ml. with water, add 1 ml. of solution (b), and dilute to 100 ml. with water.

*Standard arsenic solution.* Dissolve 0.132 g. of arsenic trioxide in 2 ml. of 1 N sodium hydroxide, dilute with water, make slightly acid with hydrochloric acid, and dilute to 100 ml. From this stock solution (1.00 mg. As per ml.) prepare a standard solution containing 0.010 mg. of arsenic per ml.

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<sup>10</sup> Another arsine-molybdenum blue method has been described by R. Milton and W. D. Duffield, *Analyst*, **67**, 279 (1942). In their procedure the arsine is absorbed in a sodium bicarbonate solution of iodine and the molybdenum blue is produced by reduction with stannous chloride. This method is slightly simpler than the one given above since no filtration is required. The authors, however, give no figures for the determination of very small quantities of arsenic (for larger quantities satisfactory recoveries of arsenic are shown to be obtained) and therefore we retain the original directions for the molybdenum blue method.

<sup>11</sup> C. J. Rodden, *J. Research Natl. Bur. Standards*, **24**, 7 (1940). This procedure was worked out with special reference to the determination of arsenic in ferrous and non-ferrous alloys, but it may be applied quite generally to inorganic samples free from strong oxidizing agents such as nitric acid.

<sup>12</sup> J. A. Scherrer, *J. Research Natl. Bur. Standards*, **16**, 253 (1936); **21**, 95 (1938).

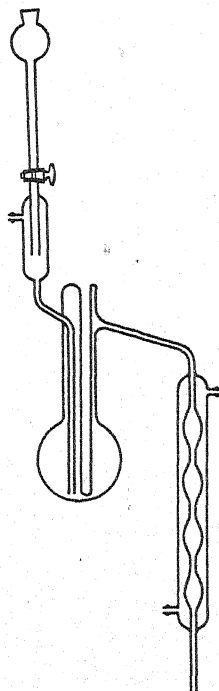


Fig. 23.—Scherrer distillation apparatus.

## ¶ Procedure

Transfer the sample to the distilling flask with concentrated hydrochloric acid. The volume of the solution in the flask may be 10–15 ml. Then add 2 ml. of hydrobromic acid and a mixture of 0.3 g. (or more if required) of hydrazine sulfate and 10 ml. concentrated hydrochloric acid. Dip the end of the condenser into 10 ml. of cold water in a small beaker. Pass a slow stream of carbon dioxide or nitrogen through the solution (2–3 bubbles per second), and boil gently until the temperature reaches 111° C. This requires about 15 minutes, and the flask will then contain approximately 10 ml. of solution.

Add 10 ml. of concentrated nitric acid to the distillate and evaporate to dryness. Then heat at 130° C. for  $\frac{1}{2}$  to 1 hour to remove nitric acid. Add 10 ml. of hydrazine sulfate-ammonium molybdate solution for each 30  $\gamma$  of arsenic and heat the solution on a steam bath for 15 minutes.<sup>13</sup> Cool, and dilute to volume with hydrazine sulfate-molybdate solution. The final solution should not contain more than 3  $\gamma$  of arsenic per ml. Obtain the transmittancy of the solution with a photometer, using a 725 or 660 m $\mu$  filter. Construct the standard curve from known amounts of arsenic treated in the same way as the unknown. Correct the results for a blank carried through all the steps of the procedure.

### *Method 2: Determination of Arsenic after Evolution as Arsine*

#### Apparatus<sup>14</sup>

The evolution vessel is a 50 ml. Erlenmeyer flask closed by a one-hole rubber stopper from which leads a tube *A* (Fig. 24) containing at its lower end one or two plugs of glass wool impregnated with lead acetate. This tube is connected by means of a short section of rubber tubing to the delivery tube *B* which is drawn down to a tip having an opening of about 0.5 mm. The absorption vessel *C* is drawn from a test tube, and should have a capacity of 8 to 10 ml. with the tapered portion of such dimensions that the 1.35 ml. of absorbing solution will have a depth of 6–7 cm. A short piece of glass tubing, *D*, having an internal diameter approximately 1 mm. greater than the external diameter of *B* is placed in the absorption vessel to break up the gas bubbles and provide more absorption surface. The apparatus should be tested for its ability to completely absorb arsine by running a known quantity of arsenic.

<sup>13</sup> If the approximate amount of arsenic is unknown add 10 ml. of hydrazine sulfate-molybdate solution, develop the color, and obtain the transmittancy of the solution. If the arsenic content exceeds 3  $\gamma$  per ml., add 10–15 ml. of reagent, develop the color and obtain the transmittancy, and proceed in this manner until the arsenic concentration is less than 3  $\gamma$  per ml.

<sup>14</sup> Instead of the apparatus described, that of C. C. Cassil and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **22**, 436 (1939) can perhaps be used. The procedure of these authors involves heating the acid solution with zinc so that the evolution time is much reduced.

### Reagents

*Stannous chloride*, 40 g. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 ml. of concentrated hydrochloric acid.

*Potassium iodide*, 15 g. in 100 ml. of water.

*Zinc*, 20 to 30 mesh, arsenic-free.

*Mercuric chloride*, 1.5 g. in 100 ml. of water.

*Potassium permanganate*, 0.03 *N*. 0.10 g. in 100 ml. of water. Discard the solution when a precipitate of manganese dioxide forms.

*Ammonium molybdate-hydrazine sulfate*. Prepare fresh daily by mixing 10.0 ml. each of solutions (a) and (b) and diluting to 100 ml. with water. *Solution (a)*: Dissolve 1.0 g. of ammonium molybdate in 10 ml. of water and add 90 ml. of 6 *N* sulfuric acid. *Solution (b)*: Dissolve 0.15 g. of hydrazine sulfate in 100 ml. of water.

### Procedure

The prepared sample must be free from substances that prevent the complete evolution of arsine.

Transfer the solution of the sample, conveniently having a volume of 25 ml. and containing not more than 15 micrograms of arsenic (20 micrograms of arsenious oxide), to the 50 ml. Erlenmeyer flask and add sufficient concentrated hydrochloric acid to make its total volume present 5 ml., 2 ml. of potassium iodide solution, and 0.5 ml. of stannous chloride solution. Allow the mixture to stand at room temperature for 15 to 30 minutes to assure the complete reduction of arsenic from the quinquevalent to the trivalent condition. Alternatively heat to 80–90° C., keep at this temperature for 5 minutes, and then cool to room temperature.

Measure 1.0 ml. of mercuric chloride solution, 0.2 ml. of 6 *N* sulfuric acid, and 0.15 ml. of potassium permanganate solution into the absorption vessel. Mix with a thin glass rod. Connect the drawn-out delivery tube to the tube passing through the rubber stopper and lower the former into the absorption vessel so that its tip nearly touches the surface of the solution. The absorbing solution should not be allowed to enter the delivery tube, for then a coating of mercury arsenide is likely to be formed later on the interior of the tube.

When all is in readiness quickly add 2.0 g. of zinc to the flask, immediately insert the stopper, and lower the delivery tube into the absorbing solution so that its tip barely touches the bottom of the vessel. Allow the gases to bubble through the solution for 25 or 30 minutes without heating the flask. At the end of this time the solution should still contain some permanganate. With larger amounts of arsenic (10 micrograms) the solu-

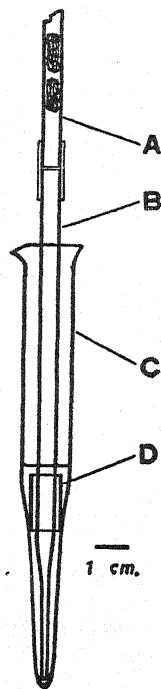


Fig. 24.—Apparatus for the absorption of arsine in the molybdenum blue method.

tion will be more or less turbid because of the separation of hydrated manganese dioxide; this does no harm. Disconnect the delivery tube from the rest of the apparatus, leave it in the absorption vessel, add 5.0 ml. of ammonium molybdate-hydrazine sulfate reagent, and mix well. Heat for 15 minutes in a water bath at 95–100°, cool, transfer the solution to a 10 or 25 ml. volumetric flask, and make up to volume with water. Filter the solution through a small plug of fine glass wool in a small funnel and reject the first portion of the filtrate.

Obtain the transmittancy of the clear solution with a photometer, using a red filter (preferably one showing maximum transmission at *ca.* 700  $m\mu$ ). In the reference cell place a comparison solution obtained as follows. Mix 1 ml. of mercuric chloride solution, 0.2 ml. of 6 *N* sulfuric acid and 0.10 ml. of potassium permanganate, and heat in a water bath for 5 minutes. Add 5.0 ml. of ammonium molybdate-hydrazine sulfate and heat for 15 minutes at 95°. Cool to room temperature, make up to the same volume as the unknown and filter.

Since Beer's law holds for the color system, the reference curve can be constructed by finding the transmittancy of one or two solutions of known arsenic concentration. Mix respectively 1.00 and 2.00 ml. of 0.001 per cent arsenic (as arsenious oxide) solution with 1.0 ml. of mercuric chloride, 0.2 ml. 6 *N* sulfuric acid and 0.10 ml. of potassium permanganate solution, and heat at 95° for 5 minutes. Then add 5.0 ml. of the molybdate-hydrazine reagent and proceed as already described for the unknown.

Correct the result for a blank carried through the procedure.

## B. THE GUTZEIT METHOD

In this old but still much-used method, arsenic (III) is reduced to arsine by the action of zinc in hydrochloric or sulfuric acid solution and the evolved gases are led over a strip of paper impregnated with mercuric bromide or chloride which is placed in a narrow tube. Instead of a paper strip, a string similarly impregnated and placed in a capillary tube may be used. Paper discs have also been employed. The stain produced is compared with a series of standard stains, generally indirectly in the case of a strip or string by making use of a graph in which the length of the stain is plotted against the quantity of arsenic.

The Gutzeit method is highly sensitive (as little as 0.01  $\gamma$  of arsenic can be detected under the proper conditions), but except for very minute amounts it is neither as precise nor as accurate as the molybdenum blue method. It is rather troublesome to carry out, and extreme care must be taken to maintain conditions constant. Thus, to mention only one factor, the rate of hydrogen evolution must be kept constant or the length of the stain will vary from one determination to another. To do full justice to

the method, a discussion of nearly monographic proportions would be required and this will not be attempted here. The reader is referred for full experimental details to the procedure given in *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists*, 5th ed., 1940, p. 390, or to the procedures of How and of Cahill and Walters.<sup>15</sup>

### C. OTHER METHODS

A number of nephelometric methods for arsenic based on the formation of colloidal dispersions of alkaloid arsenomolybdates have been described. Cocaine,<sup>16</sup> strychnine,<sup>17</sup> and quinine<sup>18</sup> have been used as reagents. These methods are inferior to the colorimetric method (IIA).

Nephelometric methods have also been based on the formation of colloidal suspensions of elemental arsenic obtained by reduction with sodium hypophosphite<sup>19</sup> in hydrochloric acid solution.

Stannous chloride in acid solution reduces arsenic, giving a reddish brown sol. The reduction takes place more easily if a minute trace of mercury is present.<sup>20</sup>

## III. Applications

### A. METALS AND ALLOYS<sup>21</sup>

#### ¶ Procedure

**Carbon Steel, Cast Iron, Ferromanganese, etc.**—Dissolve 0.1 g. of sample in 10 ml. of 1:1 nitric acid, evaporate the solution to dryness on a hot plate at a temperature not exceeding 130°. Cool, add 5 ml. of concentrated hydrochloric acid, and transfer the solution to the Scherrer distilling apparatus with the aid of 10 ml. of hydrochloric acid. Add hydrobromic acid and hydrazine sulfate as described in the directions on p. 141, distil, and finish the determination according to Method 1 above.

**High-chromium Steel.**—Dissolve 0.1 g. in a mixture of 5 ml. of concentrated nitric and 5 ml. of concentrated hydrochloric acids. Evaporate to dryness and proceed as in the case of carbon steel.

**Brass, Bronze, and Bearing Metals.**—Dissolve 0.1 g. of sample in 5 ml. of concentrated nitric acid, cool, add 8 ml. of 1:1 sulfuric acid and evaporate to fumes of sulfuric acid. Cool, add 5 ml. of water, transfer the solution

<sup>15</sup> A. E. How, *Ind. Eng. Chem., Anal. Ed.*, **10**, 226 (1938); Sister Emily Cahill and Sister Louisella Walters, *ibid.*, **14**, 90 (1942).

<sup>16</sup> H. Kleinmann and F. Pangritz, *Biochem. Z.*, **185**, 14 (1927).

<sup>17</sup> L. Belladen, U. Scazzola and R. Scazzola, *Ann. chim. applicata*, **23**, 517 (1933).

<sup>18</sup> D. Chouchak, *Ann. chim. anal. chim. appl.*, **4**, 138 (1922).

<sup>19</sup> M. Delaville and J. Belin, *Bull. soc. chim. biol.*, **9**, 91 (1927).

<sup>20</sup> W. B. King and F. E. Brown, *Ind. Eng. Chem., Anal. Ed.*, **5**, 168 (1933).

<sup>21</sup> C. J. Rodden, *J. Research Natl. Bur. Standards*, **24**, 7 (1940).

to the distilling flask with hydrochloric acid and proceed as described on p. 141.

**Pig Lead.**—To 5 g. of sample in a 400 ml. beaker add 100 ml. of 1:3 nitric acid and warm until the lead has all dissolved. Cool, add 15 ml. of concentrated sulfuric acid, and evaporate to dense fumes. Add 20 ml. of water to the cold mixture and transfer to the distilling flask with 50 ml. of concentrated hydrochloric acid. Add 10 ml. of hydrobromic acid and 1 g. of hydrazine sulfate with an additional 50 ml. portion of hydrochloric acid. Catch the distillate in 10 ml. of water contained in a 250 ml. beaker. Distil until approximately 90 ml. of distillate have been collected. Add 30 ml. of nitric acid to the distillate, evaporate to dryness on the steam bath and complete the determination as described on p. 141.

## B. SOILS<sup>22</sup>

### ¶ Procedure

Acid-soluble arsenic in soils is determined by the following procedure.

Transfer 5 g. of air-dry soil to a 200 ml. Kjeldahl flask, add 20 ml. of sulfuric acid, mix well, and then add 5 ml. of nitric acid and 0.1 g. of potassium chlorate. Heat gently at first and then more strongly until the solution boils; digest at this temperature until all organic matter is destroyed, adding more nitric acid if necessary. Cool, dilute the solution with 50 ml. of water and boil until fumes of sulfur trioxide are given off. Repeat this operation twice to expel all nitric acid. Dilute the solution in the flask with water and decant into an all-glass distilling apparatus (Fig. 23), rinsing the residue with water; an aliquot portion may of course be taken if thought desirable. Add hydrochloric acid, hydrobromic acid and hydrazine sulfate to the distilling flask, distil as already described (p. 141), and finish the determination according to the directions in the general procedure.

## C. SILICATE ROCKS<sup>23</sup>

The determination of the minute amounts (0.000n per cent) of arsenic usually occurring in silicate rocks has not been investigated as thoroughly as might be desirable but the following method has been shown to give fairly satisfactory results for the very small quantities of arsenic encountered. Approximately 80 per cent of the arsenic present in the sample is recovered, the remainder apparently being lost in the decomposition.

### ¶ Procedure

Mix and fuse 0.50 g. of 100-mesh sample with a mixture of 1.0 g. sodium

<sup>22</sup> *J. Assoc. Official Agr. Chem.*, **18**, 62, 207 (1935); see also W. O. Robinson, M. C. Dudley, K. T. Williams, and H. G. Byers, *Ind. Eng. Chem., Anal. Ed.*, **6**, 274 (1934).

<sup>23</sup> Based on unpublished work of the author.

carbonate and 50 mg. sodium nitrate. Disintegrate the melt with water, add 2.5 ml. of 60–70 per cent perchloric acid and 5 ml. of hydrofluoric acid. Evaporate to a paste, add a few ml. of water, evaporate to dryness, and heat until fumes of perchloric acid cease to come off. Transfer the residue with 25 ml. of water to a 50 ml. Erlenmeyer flask, add 5 ml. of concentrated hydrochloric acid and heat to about 80°. A practically clear solution should be obtained. Then add potassium iodide and stannous chloride and finish the determination as described on p. 142. The results are low and a more correct value for arsenic can be obtained by multiplying the apparent arsenic content by 10/8. Preferably the latter factor is determined by each analyst for his particular working conditions.

#### D. SULFIDE MINERALS

The finely powdered sample is brought into solution with a mixture of hydrochloric and nitric acids (*cf.* p. 381) or nitric acid alone, and the excess of nitric acid is expelled by addition of sulfuric acid and evaporation to thick fumes. The arsenic is then distilled as the trichloride as described on p. 141.

#### E. BIOLOGICAL MATERIALS

The destruction of organic material must be done with suitable precautions to prevent loss of arsenic. A strong oxidizing wet attack with a mixture of nitric and sulfuric acids or of nitric-sulfuric-perchloric acid is usually employed for most organic samples. Charring or browning of the sample is to be avoided as possibly leading to loss of arsenic as arsenious oxide or as arsenious chloride if chloride is present. The liquid which is boiled off in the first part of the digestion is preferably condensed and returned to the mixture for the recovery of any volatilized arsenic. If the digestion is carefully carried out, the loss of arsenic is negligible.<sup>24</sup>

In special cases, decomposition of the sample in a bomb or in a stream of oxygen may be desirable.<sup>25</sup> Oils, fats, tobacco,<sup>26</sup> and certain other materials are hard to decompose completely by wet oxidation.

Two procedures for the destruction of organic material are given below,

<sup>24</sup> Under conditions similar to those of the procedure above, D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, **13**, 915 (1941), found that the distillate from the digestion of 100 ml. of urine containing 4 mg. of arsenic showed 12  $\gamma$  of arsenic, corresponding to a loss of 0.3 per cent.

<sup>25</sup> Consult, for example, F. P. Carey, G. Blodgett, and H. S. Satterlee, *Ind. Eng. Chem., Anal. Ed.*, **6**, 327 (1934), and R. E. Remington, E. J. Coulson, and H. von Kolnitz, *ibid.*, **6**, 280 (1934).

<sup>26</sup> Pyridine and other nitrogen ring compounds resist oxidation and interfere by inhibiting the evolution of arsine. See C. R. Gross, *Ind. Eng. Chem., Anal. Ed.*, **5**, 58 (1933).



the first involving the use of nitric-sulfuric-perchloric acid, the second the use of nitric-sulfuric acid.

#### ¶ Procedure 1<sup>27</sup>

The decomposition is carried out in a special 1-liter round-bottomed Pyrex flask having three necks. One neck is connected to a vertical condenser for downward distillation, and the other two necks are fitted with funnels for the addition of acids. All the necks should be ground for standard taper connections.

Transfer a suitable weight of sample (*e.g.*, 10 g. of a solid) to the decomposition flask, and add 15 ml. each of concentrated sulfuric and nitric acids. Mix and heat to foaming or boiling. Add concentrated nitric acid dropwise from one funnel while the solution is being concentrated by boiling. Catch the distillate in a flask. When the sample has been completely dissolved, and 25 ml. or more of nitric acid has been added, add 5 ml. of 70 per cent perchloric acid dropwise from the second funnel, meanwhile continuing the addition of nitric acid. The latter must be added at such a rate that the solution does not turn brown at any time. Continue the digestion with the addition of nitric acid until the solution is colorless. The distillate may be returned to the flask at this stage if there is reason to believe it may contain arsenic. Discontinue the addition of nitric acid and heat for one-half to one hour to destroy completely organic nitrogen compounds and to expel nitric acid. Finally drive off perchloric acid by heating to strong fumes of sulfuric acid.

Transfer the cold liquid to a volumetric flask of suitable size (50 ml. is usually best) and make up to the mark with water. Arsenic may now be isolated and determined by either Method 1 or Method 2 under IIA. Method 2 is more rapid and simple, and is recommended. The aliquot taken should contain not more than 15  $\gamma$  of arsenic. A blank must be run.

#### ¶ Procedure 2<sup>28</sup>

Transfer 5 to 50 g. of sample to an 800 ml. Kjeldahl flask of Pyrex (arsenic-free) supported on an asbestos mat with a 2-inch hole. Add 25 to 50 ml. of nitric acid and then, cautiously, 20 ml. of sulfuric acid. Warm gently, discontinuing the heating if foaming becomes serious. When the reaction has slackened heat carefully, rotating the flask to prevent caking of the sample on the glass exposed to the flame. Add nitric acid in small amounts from time to time to maintain oxidizing conditions. The solution should not be allowed to remain brown for any length of time. Continue the digestion until all organic matter has been destroyed, and fumes

<sup>27</sup> H. J. Morris and H. O. Calvery, *Ind. Eng. Chem., Anal. Ed.*, **9**, 447 (1937).

<sup>28</sup> *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists*, 1940, p. 391.

of sulfuric acid are evolved. The solution should be colorless or nearly so. Cool, add about 75 ml. of water and 25 ml. of saturated ammonium oxalate solution, and evaporate until fumes of sulfuric acid appear. Cool and dilute the solution to 50 or 100 ml. in a volumetric flask.

Take a suitable aliquot of the solution and isolate and determine arsenic by either Method 1 or Method 2. The latter method is recommended as being simpler and more rapid. Correct the result for a blank run through the procedure.

## CHAPTER VIII

### BARIUM

#### I. Separations

For the isolation of barium, chief reliance is placed on the slight solubility of the sulfate and the chromate (0.29 mg.  $\text{BaSO}_4$  and 0.46 mg.  $\text{BaCrO}_4$  in 100 ml. of water at  $30^\circ$ ), whose precipitation may be made more complete by the addition of alcohol or acetone. Precipitation of the chromate requires a nearly neutral medium, whereas the sulfate may be successfully separated from a slightly acid solution if an excess of sulfate is present. Isolation of barium as sulfate has the disadvantage that in order to bring barium into solution the precipitate must be fused with sodium carbonate and the melt leached with water to obtain barium carbonate which is then dissolved in acid after washing.

Lead will be precipitated or coprecipitated with barium sulfate and chromate, and strontium with barium sulfate. A fair separation of barium from strontium<sup>1</sup> can be effected by the use of chromate as precipitant because of the relatively high solubility of strontium chromate<sup>2</sup> (96 mg.  $\text{SrCrO}_4$  in 100 g. of water at  $25^\circ$ ). Double precipitation is necessary if an appreciable amount of strontium is present. Calcium chromate is very soluble (18.2 g.  $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$  in 100 ml. of solution at  $45^\circ$ ). In the presence of lead it is best first to separate this metal electrolytically if it is present in appreciable amounts, and then to extract the solution with dithizone, after making alkaline, to remove any residual traces of lead.<sup>3</sup>

#### II. Methods of Determination

##### A. THE CHROMATE METHOD<sup>4</sup>

Barium may be determined indirectly by precipitating as the chromate, dissolving the washed precipitate in acid, and comparing the color with an acidified chromate solution, preferably obtained by dissolving barium chromate precipitated from a known amount of barium. The weakness of the method lies in the appreciable solubility of barium chromate, especially in the presence of foreign salts, and the nonspecificity of the reac-

<sup>1</sup> A. Skrabal and L. Neustadl, *Z. anal. Chem.*, **44**, 742 (1905).

<sup>2</sup> T. W. Davis, *Ind. Eng. Chem., Anal. Ed.*, **14**, 709 (1942).

<sup>3</sup> From the similarity in the ionic radii of barium and lead (1.43 and 1.32 Å. respectively) it may be expected that lead chromate or sulfate can be used to gather small amounts of barium.

<sup>4</sup> H. A. Frediani and B. J. Babler, *Ind. Eng. Chem., Anal. Ed.*, **11**, 487 (1939).

tion (precipitation of lead and possibly strontium). Separation and concentration of the barium will frequently be necessary before the method can be applied. Double precipitation usually suffices to separate barium from strontium.

Data on the performance of the method for trace quantities of barium are meager and the procedure must be given in a brief generalized form. A thorough study of the method is greatly needed, especially since it is the only satisfactory one at present for the colorimetric determination of barium.

### ¶ Procedure

Add 0.05 ml. of glacial acetic acid and 5 ml. of 25 per cent ammonium acetate solution to the neutral sample solution of appropriately small volume. Heat to boiling and add a moderate excess of 10 per cent ammonium or potassium chromate solution. Allow the solution to cool to room temperature and filter through a small sintered-glass or porous porcelain filter crucible (or use a filter stick, p. 366). Wash with cold water to remove all excess chromate. Dissolve the precipitate in 5 ml. of 4 *N* hydrochloric acid and dilute the solution to a convenient volume. Compare the solution in a Duboscq colorimeter against a similar one containing a comparable amount of barium chromate or determine the transmittancy with a photometer. Use a blue filter (maximum transmission  $< 500 \text{ m}\mu$ ).

In the presence of more than an equal amount of strontium, dissolve the precipitate of barium chromate in dilute hydrochloric acid, neutralize the solution with ammonia, and add ammonium acetate solution equal to about one-tenth the volume of the solution. Heat to boiling, add a drop or two of ammonium chromate, allow the solution to cool to room temperature and proceed as before.

**Note:** The chromate in the barium chromate precipitate can also be determined with diphenylcarbazide after solution in dilute hydrochloric acid (see p. 195).

### B. OTHER METHODS

Tannic acid (10 per cent aqueous solution) gives a transitory yellow or yellow-green color with an alkaline solution of barium, strontium, and calcium.<sup>5</sup> The colored barium salts of rhodizonic acid<sup>6</sup> and tetrahydroxyquinone are too soluble to be of much value in colorimetric trace analysis.

It may be expected that barium can be determined turbidimetrically or nephelometrically as barium sulfate but no data are available.

<sup>5</sup> Ammer and Schmitz, *Wasser*, 8, Part II, 161 (1934); *Chem. Abstracts*, 29, 4285 (1935).

<sup>6</sup> Friedrich and Rapoport, *Mikrochemie*, 14, 41 (1933).

## CHAPTER IX

### BERYLLIUM

#### I. Separations

The methods for the determination of beryllium described below require the absence of iron, manganese, magnesium, and other metals giving hydroxides insoluble in strongly basic solution. The separation of these metals by precipitation or fusion with sodium hydroxide is only successful if the treatment is repeated once or twice, since there is strong coprecipitation of beryllium hydroxide with the hydroxides mentioned. If the ratio of these metals to beryllium is very unfavorable ( $> 10,000$ ) even two or three precipitations or fusions may not give a satisfactory recovery of beryllium. In the case of iron and manganese, a better separation is obtained if these are precipitated as sulfides. The nearly neutral sample solution (5 ml.) containing up to 50 mg. of iron is added dropwise with vigorous stirring to about 10 ml. of a hot sodium hydroxide-sodium sulfide solution (10 per cent of each). The mixture is digested on the steam bath for an hour before filtration, and dilute sodium hydroxide-sulfide solution is used for washing.<sup>1</sup>

The separation of beryllium from aluminum is not necessary in the fluorimetric method with morin as reagent (IIA) and rarely in the quinalizarin colorimetric method (IIB). However, if such separation should be required, aluminum as well as ferric iron can be precipitated in acetic acid-acetate medium ( $pH$  ca. 5) with 8-hydroxyquinoline. Beryllium shows but little tendency to be carried down in the quinolate precipitate. The excess hydroxyquinoline in the filtrate can be destroyed with sulfuric-nitric acid after evaporation to a small volume.

The isolation of beryllium as hydroxide by precipitation with ammonia is being investigated. The results obtained indicate that less than 0.1  $\gamma$  of beryllium remains in solution after ammonia precipitation from a volume of 25 ml. in the presence of 3 mg. of aluminum. If ferric iron is reduced with hydroxylamine hydrochloride and mercaptoacetic acid is added to form a complex with ferrous ion, most of the latter remains in solution in the ammonia precipitation.

Electrolysis with a mercury cathode should be a useful method for the

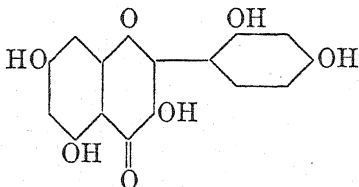
<sup>1</sup> The amount of beryllium retained in the iron or manganese sulfide is usually less than 10 per cent of the whole, and it is frequently satisfactory to omit the reprecipitation. In this case it is advantageous to make the mixture up to volume (25-50 ml.) before filtration to avoid washing the precipitate.

elimination of many interfering metals from a solution in which beryllium is to be determined.

## II. Methods of Determination

### A. THE MORIN METHOD (FLUORIMETRIC)

In sodium hydroxide solution, morin, a tetrahydroxy flavanol having the formula



yields a compound with beryllium which shows a strong yellow-green fluorescence.<sup>2</sup> This reaction may be made the basis of a very sensitive fluorimetric method for the determination of beryllium.<sup>3</sup> As little as 0.001 p.p.m. of Be in solution can be detected. Metals yielding slightly soluble hydroxides must naturally be separated before the determination can be made.

With the exception of lithium, calcium and zinc, the metals not precipitated by sodium hydroxide do not interfere. Lithium gives a weak fluorescence with morin in basic solution which is approximately one-thousandth as strong as the beryllium fluorescence. Zinc also fluoresces weakly in basic solution, but can easily be prevented from interfering by the addition of cyanide. The fluorescence of small amounts of calcium can be destroyed by the addition of sodium pyrophosphate. Certain of the rare earth hydroxides and also scandium hydroxide are sufficiently soluble in excess sodium hydroxide solution to yield a distinct fluorescence with morin. It should also be mentioned that small quantities of copper, silver and gold in basic solution oxidize morin and prevent the determination of beryllium; the same is true of manganese as manganate, but the latter is readily destroyed, for instance by heating with alcohol.

Aluminum does not interfere as long as sufficient sodium hydroxide is present to keep aluminum hydroxide in solution. Silicate, phosphate, fluoride and borate are without effect. Chromate except in minute amounts must be absent because it diminishes or destroys the beryllium fluorescence.

The intensity of the fluorescence given by beryllium depends upon the sodium hydroxide concentration, being less at high concentrations, and

<sup>2</sup> H. L. J. Zermatten, *Proc. Acad. Sci. Amsterdam*, **36**, 899 (1933); E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 762 (1940).

<sup>3</sup> E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 674 (1940)

consequently the alkalinity must be controlled. The intensity of the fluorescence decreases slowly on standing.

### Special Solutions

*Sodium hydroxide*, 1 or 2 *N*.

*Sodium pyrophosphate*, saturated aqueous solution.

*Morin*, 0.02 per cent in ethyl alcohol or acetone. The solution may be kept for months.

*Standard beryllium solution*, 0.00050 per cent. Dissolve 0.0246 g. of  $\text{BeSO}_4 \cdot 4 \text{H}_2\text{O}$  (tested purity) in water, add 1.0 ml. of concentrated hydrochloric acid and dilute to 250 ml. with water. The standard solution may also be prepared from pure  $\text{BeO}$ , by fusing the latter with potassium pyrosulfate and dissolving the melt in 0.1 *N* sulfuric acid.

### ¶ Procedure

The following directions apply to the determination of beryllium in a solution free from metals precipitated by sodium hydroxide in excess. For the separation of beryllium from such elements see p. 151 and p. 155. Lithium in appreciable amounts must be absent. Calcium should not exceed 1 part in 10,000 of solution.

The sample solution may conveniently have a volume of about 5 ml. and may contain 0.1 to 0.8  $\gamma$  of beryllium if the determination is to be made by the standard series method. A flat-bottomed tube or vial ( $2 \times 7$  cm.) may be used to hold the solution. Add 2.0 ml. of sodium pyrophosphate solution and sufficient sodium hydroxide to make its concentration about 0.1 *M* if metals not precipitated with alkali are present. If aluminum, lead, etc. are present add sufficient hydroxide to completely dissolve the precipitate first obtained. If zinc is present add 1 or 2 ml. of 5 per cent potassium cyanide (sufficient for a few milligrams of zinc). Then add 0.10 ml. of morin solution. Treat similarly a series of standards, containing the same concentration of sodium hydroxide as the sample and having the same volume, and compare in ultraviolet light. A mercury glow lamp with a purple Corex shell is a satisfactory source of ultraviolet radiation. The tubes or vials are held vertically directly above the lamp and examined transversely. Solutions differing 10 per cent in beryllium concentration show a perceptible difference in fluorescence.

The comparison may be made in strong daylight (preferably direct sunlight) against a dark shaded background if the amount of beryllium present is greater than 0.1  $\gamma$ . In this case increase the volume of morin to 0.5 ml. Prolonged exposure of the solutions to sunlight should be avoided.

### B. THE QUINALIZARIN METHOD<sup>4</sup>

Quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) yields a blue color with beryllium in sodium hydroxide solution; in the absence of beryllium

<sup>4</sup> H. Fischer, *Z. anal. Chem.*, **73**, 54 (1928).

the dye has a violet color in basic solution. Beryllium can thus be determined by the mixed-color method, *i.e.*, treating the alkaline solution with a sufficient excess of reagent to furnish a blue-violet color whose hue can then be matched in a standard series or by colorimetric titration. Aluminum in comparatively large amounts does not interfere, nor in general those metals yielding hydroxides soluble in excess sodium hydroxide with the exception of relatively much zinc which also gives a blue color. Metals forming hydroxides insoluble in alkali hydroxide must mostly be absent, notably iron and magnesium.<sup>5</sup> Copper, zinc, and nickel may be rendered harmless by the use of potassium cyanide. Phosphate does not interfere. The concentration of sodium hydroxide influences the hue of the solution, and substances such as ammonium salts which alter the pH must not be present in appreciable amounts. The solution may conveniently be 0.25 *N* in sodium hydroxide, but in the presence of aluminum the alkali concentration may be increased to 0.5 *N* to keep this element in solution.

Quinalizarin is unstable in strongly basic solution (slow fading of the color). The beryllium quinalizarin compound is rather stable, so that on standing the hue of a solution containing excess quinalizarin changes from the violet to the blue side. Therefore the color comparison should be made soon after the addition of the quinalizarin.

#### Reagent

*Quinalizarin, 0.01 per cent in acetone.* Shake 10 mg. of finely powdered quinalizarin with 100 ml. of acetone until all or nearly all of the powder has dissolved. The substance goes into solution slowly. Decant off the clear supernatant liquid and store in the dark. The solution is quite stable.

#### Procedure

The sample solution may conveniently have a volume of 5 to 10 ml. and may contain from 1 to 5  $\gamma$  of beryllium.<sup>6</sup> Add sufficient sodium hydroxide solution to make its concentration 0.2 to 0.3 *N*; in the presence of relatively much aluminum the alkali concentration may be increased to 0.5 *N* or more. Prepare a series of standards having the same volume and sodium hydroxide concentration as the unknown. Add 1.0 ml. of quinalizarin solution and compare without undue delay in flat-bottomed tubes (1.8  $\times$  15 cm.). Alternatively make the comparison by colorimetric titration, adding 0.005 per cent beryllium solution from a microburet to a solution having the same volume as the unknown and containing the same amounts of quinalizarin and sodium hydroxide, until the hues of the two solutions match.

<sup>5</sup> It may be mentioned that the rare earths, zirconium and thorium in very low concentrations yield blue colors with quinalizarin and sodium hydroxide (A. S. Komarovskiy and I. M. Korenman *Z. anal. Chem.*, **94**, 247 (1933)) just as does magnesium.

<sup>6</sup> Under the conditions described 0.5  $\gamma$  of beryllium can readily be detected.



### C. THE CURCUMIN METHOD<sup>7</sup>

In faintly alkaline solution beryllium hydroxide adsorbs curcumin, giving an orange-red lake. A blank shows a yellow to brown color. Metals precipitated by ammonia must not be present. Fluoride and magnesium reduce the color intensity. The method has not been studied in detail.

#### ¶ Procedure

To 10 ml. of slightly acid or neutral solution containing 0.05 to 1 part per million of beryllium, add 0.05 ml. of a 0.1 per cent alcoholic solution of curcumin, 0.5 ml. of 4 *N* ammonium chloride solution, and 0.5 ml. of 4 *N* ammonia. Compare against a series of standards prepared simultaneously.

### III. Special Applications: Determination of Traces of Beryllium in Silicates<sup>8</sup>

The following procedure is generally applicable to silicates or silicate rocks containing not more than approximately 10 per cent of  $\text{Fe}_2\text{O}_3 + \text{FeO} + \text{MgO} + \text{CaO} + \text{TiO}_2$ . With larger amounts of these oxides a considerable quantity of beryllium remains in the leached residue after two fusions with sodium hydroxide.<sup>9</sup> The lithium oxide content of the sample must not exceed 0.1 per cent when a 0.2 g. sample is taken. Chromic oxide should not exceed 0.02 per cent. In silicic rocks having the composition of a typical granite, 0.0005 – 0.001 per cent of beryllium can be determined to within  $\pm 0.0001$  per cent. By suitable modification of the procedure it should be possible to determine beryllium under more unfavorable conditions.

#### ¶ Procedure

Transfer 0.20 gram of the finely powdered sample containing from 0.0001 to 0.002 per cent of beryllium to a nickel crucible in which 1.0 gram of sodium hydroxide has been fused and allowed to cool. For higher percentages of beryllium the size of sample should be reduced proportionately, but the amount of sodium hydroxide should be maintained at 1.0 gram. Heat to fusion and maintain at a temperature of about 500° C. for 5 minutes or until the sample has been decomposed. Allow the crucible to cool to room temperature, and add 8 to 10 grams of ice. If the melt is green add 2 or 3 drops of alcohol. Disintegration of the melt can be hastened consid-

<sup>7</sup> I. M. Kolthoff, *J. Am. Chem. Soc.*, **50**, 393 (1928).

<sup>8</sup> E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 674 (1940).

<sup>9</sup> This statement holds for materials containing very small amounts of beryllium (thousandths and ten thousandths of a per cent) which require the taking of a fairly large sample. When the beryllium content is higher, a smaller sample can be taken and then the combined content of the oxides mentioned may be considerably higher than 10 per cent, since the absolute amount of the latter will be less and a smaller fraction of the beryllium should be retained in the residue.

erably by stirring or agitating the liquid. When disintegration is complete and manganese has been reduced, transfer the mixture to a small (30 ml.) beaker, add sufficient water to make the volume 20 ml. and stir. Filter through a small (7-cm.) retentive filter paper into a 25 ml. volumetric flask. Wash the residue and the paper with small portions of water, make up the filtrate to 25 ml., and mix.

Ignite the paper and its contents in a platinum crucible, transfer the residue to a nickel crucible, grind the solid to a fine powder with a glass rod, add 1.0 gram of sodium hydroxide, and fuse as before. Treat the melt as described above and finally make up the filtrate and washings to 25 ml. A third fusion will be unnecessary in most cases, but may be carried out as a precautionary measure.

TABLE 18  
DETERMINATION OF BERYLLIUM IN SILICATES BY THE MORIN METHOD  
AFTER DOUBLE FUSION WITH SODIUM HYDROXIDE<sup>a</sup>

Sample	Be present <sup>b</sup> %	Be found %
Synthetic acid rock.....	0.0005	0.0005
Synthetic acid rock.....	0.0010	0.0011
Granite.....	0.0015	0.0014
Granite.....	0.0030	0.0027
Granite.....	0.0055	0.0050
Synthetic basic rock.....	0.0010	0.0005
Diabase.....	0.0020	0.0012
Vesuvianite (0.01 g. sample).....	0.060	0.055

<sup>a</sup> 0.2 g. samples.

<sup>b</sup> Includes Be originally present and that added.

Determine beryllium separately<sup>10</sup> in the filtrates from the two fusions by taking 5 ml. of the solution made up to 25 ml., adding 2 ml. of saturated sodium pyrophosphate and 0.10 ml. of morin solution (0.02 per cent in alcohol or acetone), together with 1 ml. of 5 per cent potassium cyanide solution if zinc is suspected to be present, and comparing against standards (containing 0.20 g. of sodium hydroxide) according to the directions given in the general procedure above.

**Note.**—If the sample contains a high proportion of iron, manganese or other metal forming a sulfide in basic solution, it may be advantageous to decompose it with hydrofluoric-sulfuric acid and precipitate these metals with sodium hydroxide-sodium sulfide (p. 151).

<sup>10</sup> The determination is made on the two filtrates separately and not combined in order to gain some idea regarding the probable amount of beryllium in the residue from the last fusion.

## CHAPTER X

### BISMUTH

#### I. Separations

The chief methods coming into consideration for the isolation of minute quantities of bismuth are those involving the use of hydrogen sulfide and of dithizone. Precipitation with hydrogen sulfide may be applied to biological materials and other samples not containing large amounts of metals giving sulfides insoluble in dilute mineral acid medium. Copper may be added as a collector if bismuth is finally to be determined by the dithizone method; possibly cadmium will serve as a collector if bismuth is determined by the iodide method. The acidity should be as low as feasible, say 0.1–0.3 *N*.<sup>1</sup>

There is some doubt concerning the completeness of extraction of bismuth with dithizone from basic citrate solutions containing high concentrations of salts. Some authors<sup>2</sup> report incomplete recovery of bismuth under these conditions. On the other hand, Haddock<sup>3</sup> gives results that apparently show complete extraction of bismuth in the presence of much citrate and even cyanide. A further study of the extraction would be desirable (effect of citrate, cyanide, and dithizone concentration, and of *pH*). The extraction of bismuth becomes less complete in strongly basic solution. Fischer<sup>4</sup> recommends a *pH* of 7–8 for the extraction with a carbon tetrachloride dithizone solution. In the presence of cyanide, the number of metals reacting with dithizone is greatly reduced and bismuth can thus be separated from copper, silver, cadmium, zinc, etc. Lead, thallium and tin (II) also react with dithizone in basic cyanide solution. A separation of bismuth from lead (and thallium) in not too greatly preponderant amounts may be based on the comparative stability of bismuth dithizonate in dilute mineral acid solutions. By extracting an aqueous solution of *pH* 3.0 a sufficient number of times with a carbon tetrachloride solution of dithizone, bismuth can be completely brought into the carbon tetrachloride phase; practically all of the lead will remain in the aqueous phase.<sup>5</sup> At *pH* 4 the extraction of lead becomes appreciable. From the equation  $\text{Bi}^{+++} +$

<sup>1</sup> The results shown in Table 19, p. 160, indicate that microgram quantities of bismuth can be isolated satisfactorily under these conditions.

<sup>2</sup> D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, **11**, 343 (1939); J. F. Reith and C. P. van Dijk, *Chem. Weekblad*, **36**, 343 (1939).

<sup>3</sup> L. A. Haddock, *Analyst*, **59**, 163 (1934).

<sup>4</sup> H. Fischer, *Angew. Chem.*, **50**, 928 (1937).

<sup>5</sup> H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **119**, 182, 184 (1940). See also p. 280 of this book.

$3 \text{ Dz} \rightleftharpoons \text{BiDz}_3 + 3 \text{ H}^+$  it is evident that both the concentration of dithizone in the organic solvent and the *pH* of the solution will have a tremendous effect on the amount of bismuth extracted.<sup>6</sup> A more exact treatment of the separation of bismuth and lead by dithizone must await the determination of the equilibrium constants of bismuth and lead dithizonates.

Bismuth diethyldithiocarbamate may be extracted with ethyl ether<sup>7</sup> from slightly acid solution. In special cases, preliminary separation of bismuth by extraction of the iodide complex with amyl alcohol-ethyl acetate may be of value (p. 163).

Bismuth may be coprecipitated as a basic salt with manganese dioxide obtained by adding potassium permanganate to a hot, very slightly acid solution containing a manganous salt.<sup>8</sup> Park<sup>9</sup> makes the precipitation in the presence of bromide (0.2 per cent) in about 0.015 *N* nitric acid solution; the *pH* of the solution after precipitation is 2–2.6. Practically all of the bismuth, together with tin, antimony and molybdenum, is found in the precipitated manganese dioxide. A second precipitation may be carried out in the filtrate to recover the remainder of the bismuth. With 0.1 mg. of bismuth in a liter of solution containing 100 g. of copper, all of the metal was found in the first manganese dioxide precipitate; with 2 mg. in the same volume, some bismuth was found spectrographically in the second precipitate but none in the third. This method permits the separation of as little as 1 p.p.m. of bismuth in copper. Bismuth may also be coprecipitated in ferric hydroxide (p. 167).

The similarity in the ionic radii of trivalent bismuth and calcium may possibly find some application in the isolation of traces of bismuth by coprecipitation with slightly soluble calcium salts.

Bismuth may be separated from lead and tin by internal electrolysis.<sup>10</sup>

Bismuth can be separated from metallic copper by volatilization in a stream of hydrogen or nitrogen at about 1000°.<sup>11</sup>

## II. Methods of Determination

When less than 10  $\gamma$  of bismuth is to be determined, the dithizone method is recommended. Its sensitivity is so great that even 1  $\gamma$  of the element

<sup>6</sup> For graphs showing percentages of bismuth extracted at various *pH*'s with various amounts of excess dithizone see C. A. Greenleaf, *J. Assoc. Official Agr. Chem.*, **24**, 341 (1941).

<sup>7</sup> S. L. Tompsett, *Analyst*, **63**, 250 (1938).

<sup>8</sup> H. Blumenthal, *Z. anal. Chem.*, **74**, 33 (1928); S. Kallman and F. Pristera, *Ind. Eng. Chem., Anal. Ed.*, **13**, 8 (1941).

<sup>9</sup> B. Park, *Ind. Eng. Chem., Anal. Ed.*, **6**, 188 (1934).

<sup>10</sup> B. L. Clarke, L. A. Wooten, and C. L. Luke, *Ind. Eng. Chem., Anal. Ed.*, **8**, 411 (1936); E. M. Collin, *Analyst*, **55**, 312, 680 (1930).

<sup>11</sup> E. W. Colbeck, S. W. Craven, and W. Murray, *Analyst*, **59**, 395 (1934); C. O. Bannister and W. M. Doyle, *ibid.*, **60**, 33 (1935).

can be determined with fair accuracy. For amounts greater than 10  $\gamma$  the iodide method will frequently be satisfactory. The dithizone method requires the separation of bismuth from other metals, especially from lead which reacts in the same manner as bismuth under the conditions of the determination, whereas the iodide method may be applied directly in the presence of small amounts of iron, lead, etc.

### A. THE DITHIZONE METHOD

The following procedure is essentially the one described by Hubbard (*loc. cit.*) for the determination of bismuth in biological material after isolation as the sulfide. The present directions call for preliminary extraction of bismuth at pH 8.5–9.0 instead of at the slightly higher value 9.5, and for the separation of bismuth from lead and thallium by extraction at pH 2.5–3.0 instead of 2.

#### Special Solutions

*Dithizone solution*, 25 mg. of dithizone in 1 liter of redistilled chloroform. Keep in the dark, preferably in an ice box. This stock solution may be diluted with redistilled chloroform to obtain the more dilute solution required in the final determination. The latter solution should be prepared shortly before use.

*Ammonium hydroxide*. Saturate cold water with ammonia gas from a cylinder, or else distil concentrated ammonium hydroxide.

*Nitric acid*, 1:100. Dilute concentrated acid (sp. gr. 1.40), redistilled from Pyrex if necessary, with 100 times its volume of water.

*Potassium cyanide*, 10 per cent weight by volume in water.

*Ammonia-cyanide solution*. Dilute 150 ml. of concentrated ammonia and 20 g. of potassium cyanide to 1 liter with water. The potassium cyanide used may be purified by shaking a 50 per cent solution with dithizone in chloroform to remove reacting heavy metals (particularly lead) and then with chloroform to remove dithizone.

*Standard bismuth solution*, 0.0010 per cent in 1:100 nitric acid. Prepare shortly before use by diluting a 0.100 per cent bismuth solution obtained by dissolving pure bismuth metal in nitric acid.

#### ¶ Procedure

**Extraction of Bismuth, Thallium and Lead (Separation from Copper and Other Heavy Metals).**—Transfer the nitric acid solution of the isolated bismuth (for the precipitation of bismuth sulfide with copper sulfide as collector see p. 169) to a 125 ml. Pyrex separatory funnel. Dilute to approximately 50 ml., add a few drops of thymol blue and 5 ml. of 10 per cent potassium cyanide solution, and adjust the pH to 8.5–9.0 with ammonia. Extract bismuth (and any lead and thallium present) by shaking with successive 5 ml. portions of dithizone. Bismuth dithizonate possesses an orange color. The last portion of dithizone should show no color change after shaking for 1 minute. Shake the aqueous solution with 2–3 ml. of chloroform and add the latter to the chloroform extracts.

Acidify the aqueous phase with 2 ml. of concentrated nitric acid and

readjust the pH to 8.5–9.0 with 1:9 ammonia. Extract with two 5 ml. portions of dithizone.

Wash the combined chloroform extracts with 25 ml. of water to remove cyanide and draw off the chloroform into another separatory funnel. Shake the aqueous phase with a few milliliters of dithizone solution and add the latter to the previous extracts. Depending upon the quantity of bismuth present as estimated from the volume of dithizone required in the extraction (5 ml. of dithizone extracts about 25  $\gamma$  of bismuth), take either an aliquot or the whole chloroform solution, containing not more than 50  $\gamma$  of bismuth for extraction with acid. Thoroughly shake the chloroform solution with two 25 ml. portions of 1:100 nitric acid, discard the chloroform phase, and shake the aqueous phase with 1–2 ml. of chloroform to remove droplets of chloroform-dithizone.

TABLE 19  
DETERMINATION OF BISMUTH BY THE DITHIZONE METHOD<sup>a</sup>

<i>In urine</i> (100 ml.)	{ Bi added, $\gamma$ .....	0	1.0	5	15	50	500
	{ Bi found, $\gamma$ .....	0.1	1.1	4.9	15	49	470
<i>In blood</i> (10 g.)	{ Bi added, $\gamma$ .....	0	1.0	5.0	15	50	
	{ Bi found, $\gamma$ .....	0.1	1.2	5.0	14.5	48	

<sup>a</sup> Representative results taken from tables given by D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, 11, 344 (1939). Bismuth was first isolated by precipitation with hydrogen sulfide (p. 169) and then determined by a procedure essentially the same as described on p. 159.

**Separation of Bismuth from Lead and Thallium.**—Add 2 or 3 drops of m-cresol purple or thymol blue to the acid extract and adjust the pH to 2.5–3.0 with 1:9 ammonia. Extract with successive 5 ml. portions of dithizone. The shaking must be thorough. Then shake the combined chloroform extracts with two 25 ml. portions of 1:100 nitric acid to bring bismuth into the aqueous phase. Draw off as completely as possible any chloroform droplets at the bottom of the funnel, and allow the latter to stand unstoppered for a short time to permit any chloroform on the surface of the solution to evaporate.

**Determination of Bismuth.**—To the 50 ml. of the acid solution add 10 ml. of ammonia-cyanide mixture and an appropriate volume of dithizone solution of suitable concentration depending upon the approximate amount of bismuth as estimated from the previous extraction:

Range of Bi $\gamma$	Dithizone concentration mg./liter	Volume of dithizone ml.	Cell length mm.
0–5	6	10	50
0–25	12	25	25
0–50	25	25	12

Shake for 15 seconds and transfer the chloroform layer (free from water droplets) to a suitable cell. Obtain the optical density of the chloroform solution, using light of wave length 505  $m\mu$ . Construct the reference curve from known amounts of bismuth in 1:100 nitric acid saturated with chloroform.

When the standard series method of comparison is used, a suitable quantity of bismuth is 1-3  $\gamma$  in about 5 ml. of 1:100 nitric acid. Shake in a glass-stoppered tube (p. 42) with about 2 ml. of 0.001 per cent dithizone solution after adding 1 ml. of ammonia-cyanide solution, and compare against standards obtained in a similar way.

### B. THE IODIDE METHOD<sup>12</sup>

The addition of an excess of a soluble iodide to an acid solution of bismuth produces a yellow to orange color. The color intensity increases with iodide concentration up to about 1 per cent potassium iodide and then remains practically constant (Wiegand, Lann and Kalich, *loc. cit.*). Beer's law is followed. The reaction is a sensitive one, but is subject to interference from a number of substances. Platinum, palladium, and, to a lesser extent, antimony and tin give colored compounds with iodide. Metals giving insoluble iodides must naturally be absent, or present in amounts not yielding a precipitate. Lead and thallous iodides carry down large quantities of bismuth, but silver and cuprous iodides show a much smaller tendency to occlude bismuth. Oxidizing agents such as ferric iron liberating iodine must be reduced or the iodine formed by them destroyed. Sulfurous acid or sulfite is frequently used for this purpose but care must be taken to avoid any large excess because, in sufficient concentration, sulfite alone produces a yellow color with iodide, probably owing to the formation of an iodo-sulfinic acid,  $I(HSO)_2$ . Hypophosphorous acid can often be used instead of sulfurous, although it acts slowly. High concentrations of acid (more than 50 per cent of sulfuric or hydrochloric acid) yield a weak yellow color in the absence of bismuth because of the formation of complex iodo acids, but dilute acids (less than 1-2  $N$ ) do not.<sup>13</sup> In 2  $N$  sulfuric acid solution the color is very slightly stronger than in 0.2  $N$  solution.

Chloride ion reduces the intensity of the bismuth color. Fluoride in high concentration also reduces the color intensity. Sulfate ion in reasonable amounts is without effect and therefore sulfuric acid is ordinarily used for acidification, but nitric acid may also be used if its concentration in the

<sup>12</sup> H. Baggesgaard-Rasmussen, K. A. Jackerott, and S. A. Schou, *Dansk. Tids. Farm.*, **1**, 391 (1927); R. C. Sproull and A. O. Gettler, *Ind. Eng. Chem., Anal. Ed.*, **13**, 462 (1941); C. J. W. Wiegand, G. H. Lann, and F. V. Kalich, *ibid.*, **13**, 912 (1941).

<sup>13</sup> L. A. Haddock, *Analyst*, **59**, 163 (1934).

solution is not too high. Cadmium in large amounts bleaches the bismuth color (formation of complex cadmium iodide) but the effect can be largely overcome by adding more iodide. A number of other elements such as arsenic and the rare earths in high concentration reduce the color intensity.

The colored product can be extracted by higher alcohols and esters. A mixture of amyl alcohol and ethyl acetate has been recommended for the purpose. The extraction procedure enables bismuth to be determined in the presence of colored ions such as nickel, cobalt, chromium, and uranium. The organic solvent solution of the bismuth-iodide compound obeys Beer's law.

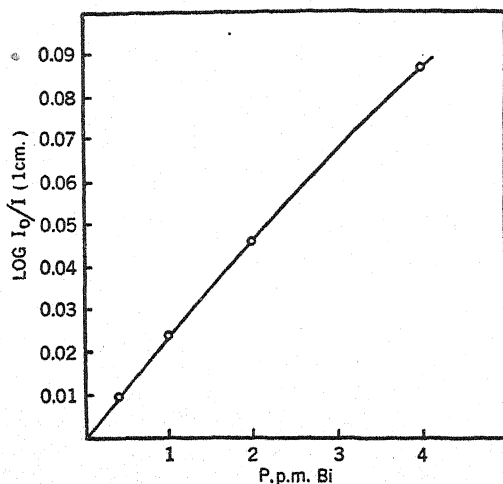


Fig. 25.—Determination of bismuth by the iodide method (aqueous solution). The slight deviation from linearity is due to the comparatively wide band of wave lengths transmitted by the blue filter used (Wratten 47). Transmittancy of the blank solution was 95.6% under the conditions.

The procedure below is similar to Haddock's<sup>13</sup>. The determination of bismuth may be made directly in the presence of considerable quantities of the alkali metals, alkaline earth metals, magnesium, manganese, zinc, cobalt, nickel, chromium, aluminum, etc. Lead and thallium do not interfere if present in such small amounts that no precipitate forms. In the presence of antimony, copper, iron, silver, etc., Haddock first isolates bismuth by extraction with dithizone from an ammoniacal cyanide solution. Some of the results obtained by Haddock in the application of the extraction procedure are given in Table 20.

#### Reagents

*Potassium iodide*, 10 per cent aqueous solution, preferably freshly prepared.

*Sulfurous acid*, 5 per cent solution of SO<sub>2</sub> in water. Dilute a saturated solution



of sulfur dioxide in water at ca. 25° with an equal volume of water. This solution must be freshly prepared.

*Hypophosphorous acid*, 30 per cent.

*Amyl alcohol-ethyl acetate*, 3:1 mixture by volume.

### ¶Procedure

The sample solution may conveniently have a volume of 10 or 20 ml and should be 1 to 2 *N* in sulfuric acid. At least 5γ of bismuth should be present. Add 0.1 ml. of sulfurous acid, or 1 ml. hypophosphorous acid, and 3 ml. of potassium iodide solution. Dilute to 25 ml. and determine the transmittancy at or near 460 mμ.

TABLE 20  
DETERMINATION OF BISMUTH BY EXTRACTION OF THE BISMUTH-IODIDE COMPOUND  
WITH AMYL ALCOHOL-ETHYL ACETATE<sup>13</sup>

Foreign Element	Bi Added γ	Bi Found γ
1g. Sb <sup>a</sup>	30	33
1g. Cu <sup>a</sup>	20	18
2g. "Di" <sup>a</sup>	10	12
1g. Fe <sup>III</sup>	10	12.8
1g. Hg <sup>a</sup>	50	50
1g. Ag <sup>a</sup>	20	20
1g. Sn <sup>IV</sup> <sup>a</sup>	20	17.5
1g. Co	10	11
1g. Ni	10	12
1g. Cr	10	12.5
1g. Zn	10	10

<sup>a</sup> Preliminary separation of bismuth with dithizone.

*Extraction Procedure.*—If the sample solution contains colored ions, extract the solution after addition of iodide, etc. with successive 2 or 3 ml. portions of amyl alcohol-ethyl acetate until the last extract is colorless or virtually so. Make up the combined extracts to a definite volume (5 ml. for 10–40 γ of bismuth, 10–15 ml. for 40–100 γ) with the organic solvent. Filter the solution through a small plug of cotton-wool, and transfer the filtrate to a suitable vessel for comparison or measurement. For less than 20 γ of bismuth, flat-bottomed tubes of approximately 1 cm. diameter may be used in comparing; for larger amounts a Duboscq colorimeter may be used. Prepare the standard solution by adding a suitable quantity of bismuth to the extracted solution and extracting as before.

*Note.*—The aqueous bismuth solution to be extracted with amyl alcohol-ethyl acetate should have a volume less than 40 ml. In general, 2 extractions will remove 5 to 20 γ of bismuth and 4 extractions 50 to 80 γ. For 100 γ, 5 extractions should be made. By adding a known amount of bismuth to the extracted sample solution

and extracting as before, any error due to slight coloration of the organic solvent resulting from a high concentration of neutral salts or from solution of small amounts of cobalt, nickel or chromium is largely compensated.

### C. THE THIOUREA METHOD<sup>14</sup>

In acid solution, thiourea forms a soluble complex with bismuth having a yellow color. The reaction is of rather low sensitivity. Silver, mercury, lead, copper, cadmium, and tin give white precipitates if present in considerable amounts, but none at low concentrations (copper is then decolorized). Ferric iron must be reduced, for example, by heating the solution with hydrazine sulfate. Antimony also gives a yellow color with thiourea. Fluoride destroys the antimony color but not that of bismuth.

Beer's law holds for the bismuth complex in the range 0.2 to 5 mg. of metal per 100 ml.

#### ¶ Procedure<sup>15</sup>

The bismuth solution should be 0.7–1.3 *N* in nitric acid and should contain no chloride. Iron must previously have been reduced to the ferrous condition. Add 10 to 12 g. of thiourea for 50 ml. of solution, warm gently to dissolve, cool to  $18 \pm 3^\circ$ , and filter through a sintered-glass crucible (G4) to remove excess thiourea and any precipitated metal complexes. Wash with saturated thiourea solution and make up to volume with the same solution. Use a filter showing maximum transmission at 460  $m\mu$  in determining the color intensity.

The solution becomes turbid on standing from the separation of sulfur, especially when lead and copper are present. This can be prevented by adding hydrazine sulfate to the solution and keeping it cool.

### D. OTHER METHODS

Among the many other methods which have been described for the colorimetric determination of bismuth the following may be noted:

1. Formation of an orange double iodide with 8-hydroxyquinoline which can be extracted with a mixture of acetone and amyl alcohol or with cyclohexanol.<sup>16</sup>
2. Formation of a yellow color with potassium thiocyanate in acid solution similar to that produced by thiourea.<sup>17</sup>
3. Precipitation of bismuth with pyrogallol or 8-hydroxyquinoline and

<sup>14</sup> C. Mahr, *Z. anal. Chem.*, **94**, 161 (1933); **97**, 96 (1934). S. L. Tompsett, *Analyst*, **63**, 250 (1938).

<sup>15</sup> C. Mahr, *Z. anal. Chem.*, **97**, 96 (1934).

<sup>16</sup> R. Sazerac and J. Pouzergues, *Compt. rend. soc. biol.*, **109**, 79, 370 (1932).

<sup>17</sup> H. Heinrichs and M. Hertrich, *Glastech. Ber.*, **1924**, 112.

subsequent reduction of phosphomolybdic acid to molybdenum blue.<sup>18</sup>

4. Formation of a colloidal suspension of bismuth sulfide in dilute acid solution in the presence of gelatine,<sup>19</sup> or in basic solution in the presence of gum arabic.<sup>20</sup>
5. Formation of a colloidal suspension of bismuth with stannite.<sup>21</sup>

### III. Applications

#### A. METALS

##### 1. Antimony, Mercury, Silver, Iron, Etc.

Haddock (*loc. cit.*) has shown that small amounts of bismuth, of the order of a few thousandths of a per cent, can be determined in the presence of these metals by separating bismuth by dithizone extraction from a basic cyanide medium and making the final determination by the iodide method (Table 20). The absence of appreciable amounts of lead and thallium is presupposed. Bismuth can thus be determined in the presence of metals forming stable cyanide complexes in alkaline solution (mercury, silver, gold and copper) as well as those not reacting with dithizone (arsenic, antimony and iron). More specific directions for determining bismuth in copper in this way are given on p. 166.

#### ¶ Procedure

Bring a 0.5 to 1 g. sample of metal ( $\text{Bi} < 0.01$  per cent) into solution by appropriate treatment with acid. If there is a possibility of a little stannous tin being present in the solution, add a small amount of a ferric salt to oxidize it to the stannic condition. Boil out oxides of nitrogen if nitric acid has been used. Add 1 to 2 g. of ammonium citrate<sup>22</sup> to the solution (volume about 25 ml.), neutralize with ammonia and add 2 g. of potassium cyanide<sup>23</sup> and 5 ml. of 10 per cent ammonia. Extract in a separatory funnel with four 15 ml. portions of 0.1 per cent (weight/volume) dithizone solution in chloroform. Combine the dithizone extracts and wash with

<sup>18</sup> M. Teitelbaum, *Z. anal. Chem.*, **82**, 366 (1930).

<sup>19</sup> F. Malengreau and G. Delrue, *Arch. intern. méd. expél.*, **1**, 35 (1924).

<sup>20</sup> T. Yamamoto, *Bull. Inst. Phys. Chem. Research Tokyo*, **13**, 1265 (1934).

<sup>21</sup> L. Malossi, *Rend. accad. sci. Napoli*, **2**, 83 (1932).

<sup>22</sup> In the presence of much iron a larger amount of citrate may be necessary. The quantity of citrate added should not be much greater than that required to keep the metals in solution when the mixture is made basic. The addition of hydroxylamine hydrochloride may be advantageous when much iron is present (prevention of oxidation of dithizone by ferricyanide).

<sup>23</sup> When much copper, silver and other metals forming cyanide complexes are present, the quantity of potassium cyanide may have to be increased to 5 or 10 g. to prevent these metals from reacting with dithizone.

two 10 ml. portions of water. Transfer the washed chloroform phase to a small Erlenmeyer flask, evaporate to dryness and add 1 ml. of concentrated sulfuric acid. Heat carefully over a small flame and add dropwise 30 per cent hydrogen peroxide until all organic matter has been destroyed.<sup>24</sup> Dilute with 15–20 ml. of water, cool, and add a dilute iodine solution in very slight excess to destroy any sulfur dioxide. Then determine bismuth by the iodide method (p. 163).

## 2. Copper

There is no dearth of procedures for the determination of minute quantities of bismuth in metallic copper, but there is some doubt about the accuracy of a number of these procedures, especially when the percentage of bismuth is less than 0.001 per cent. Most of the methods call for the final determination of bismuth by the iodide method after isolation of bismuth by coprecipitation with collectors such as hydrous manganese dioxide or ferric hydroxide,<sup>25</sup> or by extraction with dithizone from cyanide medium. In one procedure copper is precipitated as cuprous iodide.<sup>26</sup> The directions given below are essentially those of the Fiscal Policy Joint Committee of the (British) Brass, Copper and Nickel Silver Industries.<sup>27</sup> The procedure is suitable for samples containing from 0.0002 to 0.005 per cent bismuth.

### ¶ Procedure

Dissolve 2 g. of drillings in 20 ml. 1:1 nitric acid in a 250 ml. Erlenmeyer flask (see Note 1 for treatment of any insoluble material). Evaporate the solution until it becomes viscous, add 3 ml. of concentrated sulfuric acid, and continue the evaporation until white fumes are evolved. Cool, add 30 ml. of water and 20 ml. of 5 per cent citric acid, and make slightly ammoniacal so as to bring all copper salt into solution (usually 12–15 ml. of ammonia of sp. gr. 0.88 are required). Cool and add 50 ml. of fresh 20 per cent potassium cyanide solution.<sup>28</sup> Transfer the solution to a 250 ml. separatory funnel, dilute to 20 ml. with water, and shake with successive 10 ml. portions of 0.1 per cent dithizone in chloroform until all the bismuth has been extracted. Usually 3 or 4 portions suffice, unless much lead is

<sup>24</sup> Sulfuric and perchloric acids may also be used for the destruction of organic matter (p. 228).

<sup>25</sup> See, for example, A. J. G. Smout and J. L. Smith, *Analyst*, **58**, 475 (1933); C. O. Bannister and W. M. Doyle, *ibid.*, **60**, 33 (1935).

<sup>26</sup> H. R. Fitter, *Analyst*, **63**, 107 (1938).

<sup>27</sup> *Analyst*, **60**, 554 (1935).

<sup>28</sup> H. Fischer, *Angew. Chem.*, **50**, 929 (1937), recommends adjusting the pH of the solution to 7–8 at this point by buffering with an ammonium salt (e.g., ammonium nitrate).

present (red extract). Finally shake the aqueous solution with 5 ml. of chloroform and add this to the combined chloroform extracts. Shake this combined solution with 50 ml. of water. Run the washed chloroform into a small (150 ml.) flask and evaporate to practical dryness.<sup>29</sup> Add 1 ml. of concentrated sulfuric acid, heat until thick fumes are evolved, cool, and add 2-3 ml. of 20-volume hydrogen peroxide. Continue the heating until the solution is colorless, adding more hydrogen peroxide if necessary. Cool and add 15 ml. of water. Filter off any residue of lead sulfate (see Note 2 for treatment of the precipitate).

Determine bismuth in the solution by the iodide method in any convenient way, for example by the photometric procedure (p. 163) after transferring the solution to a 25 ml. volumetric flask. Alternatively transfer the solution to a color comparison tube, add sulfurous and hypophosphorous acids and potassium iodide (*cf.* p. 163). In a second tube prepare a solution having the same composition as the sample and add a dilute standard bismuth solution until the odors match.

**Notes.**—1. Any metastannic acid or other insoluble material remaining after solution of the sample should be fused with potassium pyrosulfate, the melt leached with dilute sulfuric acid and the filtered solution added to the main solution.

2. Any lead sulfate precipitated should be filtered off, ignited, and dissolved in 10 ml. of hot concentrated hydrochloric acid. The resulting solution is cooled, 1 g. of tartaric acid, and 1 ml. each of concentrated nitric and sulfuric acids are added. The mixture is evaporated to expel the volatile acids (until red fumes cease to come off). Fifteen ml. of water are added, the solution is filtered, and the filtrate combined with the main solution.

### 3. Lead

#### ¶ Procedure<sup>30</sup>

Dissolve 20 g. of sample in a mixture of 25 ml. nitric acid and 50 ml. of water. Add 30 ml. of hydrochloric acid to precipitate lead chloride,<sup>31</sup> cool to at least 20°, filter and wash the precipitate with cold 1:1 hydrochloric acid. To the filtrate add 5 mg. of iron as ferric salt followed by 20 ml. of 20 per cent ammonium acetate solution. Add sodium hydroxide solution until a small amount of lead hydroxide is precipitated, and just bring the latter into solution by the dropwise addition of hydrochloric acid, finally adding an excess of 1 ml. of the acid. Filter off the ferric hydroxide immediately on an asbestos mat and wash three times with water. Dissolve the precipitate in 50 ml. of warm 1:20 sulfuric acid containing 3 g.

<sup>29</sup> Fischer, *loc. cit.*, recommends that the dithizone extracts be shaken with 10 per cent sulfuric acid to transfer the bismuth to the aqueous phase. The latter is then evaporated to a small volume, and traces of organic material are destroyed by adding hydrogen peroxide and heating to fumes of sulfuric acid.

<sup>30</sup> R. G. Robinson, *Analyst*, **64**, 402 (1939).

<sup>31</sup> Precipitation of lead as sulfate leads to large losses of bismuth.

of tartaric acid, allowing the solution to flow slowly through the filter. Wash twice with a little water. Treat the filtrate and washings with 5 ml. of hypophosphorous acid (sp. gr. 1.135) and dilute with water to 100 ml. Pour the solution into a dry flask containing 1.5 g. of potassium iodide. Heat to 70°, cool to 20° and determine the color intensity of the solution.

**Notes.**—1. With the acidity specified above, antimony in small amounts (5 mg.) does not interfere in the colorimetric determination. At higher acidities antimony gives a yellow color.

2. The accuracy of the method is attested by the fact that samples of lead containing 0.0005, 0.0010 and 0.0015 per cent of bismuth gave the respective values 0.0005, 0.0011 and 0.0014 per cent.

## B. BIOLOGICAL MATERIALS

If the bismuth content of the sample is greater than 5 or 10 p.p.m. the iodide method can generally be applied directly after destruction of organic matter. This method has the advantage of simplicity and rapidity. Such small amounts of lead, copper, iron and other metals as are likely to be present in most samples will not interfere. On the other hand, if the bismuth content is so low that the final aliquot of solution contains less than 10–20  $\gamma$ , the dithizone method is probably preferable.

The destruction of organic matter is usually effected by digestion with sulfuric and nitric acids, often together with perchloric acid.<sup>32</sup> Typical procedures have been given by Wiegand, Lann, and Kalich<sup>33</sup> and by Sproull and Gettler<sup>34</sup>. The procedure given below for the acid digestion is similar to that of the latter authors.

### ¶ Procedure

**1. Iodide Method.**—*Tissue.* Transfer 10 g. of sample to an Erlenmeyer flask and add 20 ml. of concentrated nitric acid. Heat on the steam bath until a clear yellow or brown solution is obtained. Cool, and if fat separates filter it off on glass wool, collecting the filtrate in a small Kjeldahl flask and washing with a little nitric acid. Add 3 ml. of concentrated sulfuric acid and evaporate to fumes of the latter. Then add dropwise a 1:2 mixture of nitric-perchloric acid and continue heating until the color

<sup>32</sup> J. Cholak, *Ind. Eng. Chem., Anal. Ed.*, **9**, 26 (1937), and D. M. Hubbard, *ibid.*, **11**, 344 (1939), decompose organic samples by digesting with nitric acid, evaporating to dryness and then heating at 450–500° C. in a muffle for several hours; if a gray ash is obtained, it is moistened with nitric acid and again ignited until it is white. When much phosphorus is present, the ash is likely to fuse and the procedure is not suitable.

<sup>33</sup> C. J. Wiegand, G. H. Lann, and F. V. Kalich, *Ind. Eng. Chem., Anal. Ed.*, **13**, 912 (1941).

<sup>34</sup> R. C. Sproull and A. O. Gettler, *Ind. Eng. Chem., Anal. Ed.*, **13**, 462 (1941).

is destroyed. Next add 0.5 ml. of 30 per cent hydrogen peroxide dropwise and boil to destroy the excess. Cool, add 5 ml. of water and evaporate to fumes of sulfuric acid. After cooling dilute with water, transfer to a 25 ml. volumetric flask, and make up to the mark. Determine bismuth in a 10 ml. aliquot according to the directions on p. 163. For low bismuth concentrations use a 2 or 5 cm. cell in obtaining the transmittancy. The standards for the establishment of the reference curve should have the same acidity as the unknown solution. For the greatest accuracy known amounts of bismuth should be added to a bismuth-free material of the same nature as the sample and carried through the procedure to obtain the standard curve.

*Urine.*—Add 5 ml. of nitric acid and 3 ml. of sulfuric acid to a 50 ml. sample, and evaporate to fumes of sulfuric acid. Then add a mixture of nitric and perchloric acids as described in the preceding paragraph and continue according to the directions given there.

**2. Dithizone Method.**—Take a sample of such size that the aliquot used for the final determination (p. 160) will contain 5  $\gamma$  or more of bismuth. Destroy organic matter by wet oxidation (see above, and footnote 32, p. 168). Adjust the acidity of the diluted digest to 0.2–0.3 *N* with the aid of 4 *N* sodium hydroxide solution. Add 1 mg. of copper to the solution (50–100 ml. in volume) to furnish copper sulfide and pass in hydrogen sulfide for one-half hour. Allow the mixture to stand overnight and filter off the precipitate on a small dense filter paper. Wash once or twice with 5 ml. of 0.1 *N* hydrochloric acid saturated with hydrogen sulfide. Transfer the filter paper to the precipitation vessel and heat gently with 10 ml. of 1:3 nitric acid to dissolve the sulfides. Filter off the disintegrated paper and sulfur by the use of a fine sintered-glass filter crucible and wash with hot dilute nitric acid. Evaporate the filtrate to a small volume to remove most of the nitric acid. Dilute with water and determine bismuth according to the directions on p. 159, using either the whole solution or an aliquot of it.

## CHAPTER XI

### CADMIUM

#### I. Separations

When it is a matter of isolating cadmium from a solution containing only small amounts of heavy metals such as copper, silver, zinc, etc., dithizone is the reagent of choice. Cadmium dithizonate may be extracted quantitatively in faintly basic solution. It is easily decomposed by shaking the organic solvent solution with dilute acid (0.01 *N* hydrochloric acid suffices for a carbon tetrachloride solution). A separation can thus be effected from copper, mercury, silver, and other metals whose dithizonates are hardly affected by weak mineral acid. The separation from cobalt in this way is quite satisfactory, but the separation from nickel is imperfect because nickel dithizonate is appreciably decomposed by the dilute acid. The great stability of cadmium dithizonate in strongly basic solutions makes possible the separation from lead, zinc, and bismuth. Cadmium can be extracted with a carbon tetrachloride solution of dithizone from an aqueous solution 1 *N* in sodium hydroxide. At this high alkalinity, the metals mentioned are extracted hardly at all, even if present in relatively high concentrations (see Table 21, p. 171). Much zinc tends to give low results. Other metals extracted with cadmium under these conditions include copper, silver, mercury, cobalt, and nickel.

Precipitation of cadmium as sulfide is a useful separation method in some instances. For complete recovery of cadmium the solution should be very slightly acid and a collector should be used.<sup>1</sup> High concentrations of the halides hinder the precipitation of cadmium sulfide in acid solution. Presumably hydrogen sulfide will provide a separation of little cadmium from much nickel and cobalt at low acidities. Fractional precipitation of cadmium sulfide may be applied to isolate cadmium from large quantities of zinc. A restricted amount of sodium sulfide is added to the solution to give a precipitate of zinc sulfide which contains virtually all of the cadmium present. The cadmium thus enriched may be separated from the zinc in the precipitate with dithizone if required.

Cadmium pyridine thiocyanate may be extracted with chloroform and a

<sup>1</sup> L. T. Fairhall and L. Prodan, *J. Am. Chem. Soc.*, **53**, 1321 (1931), in isolating cadmium from a solution of acid-digested organic material make the hydrogen sulfide precipitation at *pH* 3 in the presence of about 2 per cent sodium citrate and a little copper salt.



separation of cadmium thus made from silver, mercury, and copper (reduced to the cuprous state).<sup>2</sup> See p. 173.

## II. Methods of Determination

### A. THE DITHIZONE METHOD

Fischer and Leopoldi<sup>2</sup> have given the following directions for the determination of cadmium with dithizone. The determination can be made directly in the presence of lead, bismuth, tin (II), and moderate amounts

TABLE 21  
DETERMINATION OF CADMIUM BY THE COLORIMETRIC DITHIZONE METHOD<sup>a</sup>

Foreign metal	Cd taken γ	Cd found γ	Error γ	Remarks
	5.6	5.8	+0.2	
	7.4	7.4	0.0	
	18.5	18.2	-0.3	
	33.3	33.0	-0.3	
50 mg. Fe (III)	7.4	7.8	+0.4	5 ml. 25% Rochelle salt
200 mg. As (V)	5.6	5.3	-0.3	
100 mg. Sb (III)	5.6	5.3	-0.3	
75 mg. Pb	5.6	5.3	-0.3	
50 mg. Bi	7.4	7.0	-0.4	1 ml. 25% Rochelle salt
25 mg. Sn (II)	5.6	5.3	-0.3	1 ml. 25% Rochelle salt
30 mg. Zn	7.4	7.0	-0.4	
60 mg. Zn	7.4	5.5	-1.9	
30 mg. Ag	7.4	7.8	+0.4	Cd separated by extraction of the pyridine thiocyanate with chloroform
30 mg. Hg (II)	7.4	7.8	+0.4	
30 mg. Cu	7.4	8.2	+0.8	
30 mg. Cu	7.4	7.8	+0.4	
25 g. Zn	0.030%	0.031%	+0.001%	Preliminary concentration of cadmium as sulfide. Determination on aliquot ≡ 1 g. Zn
	0.0074%	0.0071%	-0.0003%	
	0.0022%	0.0021%	-0.0001%	

<sup>a</sup> Selection of figures from data of H. Fischer and G. Leopoldi, *Mikrochim. Acta*, **1**, 30 (1937), especially from the lower ranges of cadmium.

of zinc (Zn:Cd less than 3000) by extracting with dithizone from an approximately 5 per cent sodium hydroxide solution. A carbon tetrachloride, not chloroform, solution of dithizone must be used if zinc is present. When copper, silver, and mercury are present, cadmium must first be separated by the pyridine-thiocyanate method already referred to. This procedure

<sup>2</sup> H. Fischer and G. Leopoldi, *Mikrochim. Acta*, **1**, 30 (1937).

does not provide for the presence of nickel and cobalt. The figures in Table 21 will give some idea of the accuracy of the method.

#### Reagents

*Dithizone*, 5 mg. in 100 ml. of carbon tetrachloride.

*Sodium hydroxide solution*, 10 per cent. The solution should be tested by diluting with an equal volume of water and shaking with dithizone. The carbon tetrachloride layer must become colorless or at most slightly yellowish.

*Sodium hydroxide solution*, 2 per cent. The solution must give no reaction with dithizone.

*Sodium potassium tartrate solution*, 20 per cent. The solution must show no reaction with dithizone when mixed with an equal volume of 10 per cent sodium hydroxide.

*Ammonium thiocyanate solution*, (a) 25 g. in 100 ml. of water, (b) 2 g. in 100 ml. of water.

*Pyridine-chloroform*. A mixture of 5 ml. of pyridine and 100 ml. of chloroform.

*Sulfurous acid*, 1 per cent  $\text{SO}_2$  in water.

*Nitric acid*, concentrated.

*Sodium acetate solution*, 5 per cent.

*Standard cadmium solution*, 0.001 per cent Cd in 0.1 *N* hydrochloric acid. Prepare fresh by diluting a stronger solution (0.01 or 0.1 per cent) obtained by weighing out pure cadmium metal.

#### ¶ Procedure

**In Pure Solution or in the Presence of the Alkali and Alkaline Earth Metals, Aluminum, Manganese, Iron, Arsenic, Antimony, Zinc, Lead, Bismuth, and Tin.**—The solution may have a volume of 5 to 10 ml. and may contain 3 to 30  $\gamma$  of cadmium. Add an equal volume of 10 per cent sodium hydroxide solution to the approximately neutral sample solution which has been treated with sufficient sodium potassium tartrate to keep metals precipitated by alkalis in solution (5 ml. of 20 per cent sodium potassium tartrate suffices to prevent the precipitation of 50 mg. of iron). Extract in a separatory funnel with small portions of dithizone until the last portion becomes colorless (see Note 3). Collect the extracts in a separatory funnel, and wash the extracted aqueous solution with a few milliliters of carbon tetrachloride.

Shake the carbon tetrachloride extract with two successive portions of 2 per cent sodium hydroxide solution having approximately one-half the volume of the carbon tetrachloride, wash once with a small volume of water, and transfer the carbon tetrachloride to a small volumetric flask (*e.g.*, 25 ml.) and make up to volume with the same solvent. Since cadmium dithizonate solution in carbon tetrachloride is not very stable, transform the complex into free dithizone by shaking with 0.5 *N* hydrochloric acid.<sup>3</sup>

<sup>3</sup> For the determination of very small amounts of cadmium, however, comparison as cadmium dithizonate is permissible and indeed preferable. See p. 175. The transmittancy may be measured at 520  $\text{m}\mu$ .

Compare against a standard solution of dithizone prepared in the same manner as the unknown or determine the transmittancy at 620  $m\mu$  with a photometer.

**In the Presence of Silver, Mercury and Copper.**—When silver and mercury are present in the sample proceed as follows. To the slightly acid solution add sufficient ammonium thiocyanate (25 per cent solution) to redissolve the silver thiocyanate first precipitated. If mercury is present, a greater excess of thiocyanate is required (approximately 5 ml. of ammonium thiocyanate per 10 mg. of mercury). Add sodium acetate solution until blue Congo paper just turns red ( $pH$  5). Extract with small portions of pyridine-chloroform totaling 15 ml. Wash the combined extracts once with an equal volume of 2 per cent ammonium thiocyanate solution.

Evaporate the chloroform extract to dryness on the water bath, add 3 ml. of concentrated nitric acid, and again evaporate to dryness. Take up the residue in 2 or 3 ml. of 1 per cent sulfuric acid, transfer to a separatory funnel, and rinse with a little water. Extract with small portions of dithizone to remove traces of silver and mercury. Dilute the aqueous solution with water to 10 ml. and determine cadmium as described above.

In the presence of copper proceed as follows. Add sodium carbonate solution to the acid sample solution until a turbidity appears and then clear the solution with a few drops of sulfurous acid. Heat nearly to boiling, add 5–6 ml. sulfurous acid (for 30 mg. Cu), boil briefly, and cool to room temperature. In this way most of the copper is reduced to the cuprous condition. Reduce the acidity of the solution by the addition of sodium acetate as already described above and add sufficient ammonium thiocyanate to dissolve the precipitated cuprous thiocyanate. Extract with chloroform-pyridine and proceed as already described. Since some copper is extracted by pyridine-chloroform, it must be removed by shaking with dithizone in acid solution before the cadmium determination.

**Notes.**—1. Cadmium dithizonate has only a limited solubility in carbon tetrachloride, and if much cadmium is present yellow flocs of the dithizonate may separate. The solubility in chloroform is much greater, and a chloroform solution of the reagent may be used except when appreciable amounts of zinc are present. The stability of cadmium dithizonate is greater in chloroform than in carbon tetrachloride.

2. If an appreciable quantity of manganese is present, hydroxylamine hydrochloride should be added to prevent oxidation of the dithizone and the obtaining of low results for cadmium.

3. When much zinc is present it may be slightly coextracted with the cadmium so that on successive extraction with dithizone a point is never reached at which the carbon tetrachloride becomes colorless. In such a case the extract must be shaken with 2 per cent sodium hydroxide solution before being added to the previous extracts. If the red color then disappears it was due to zinc dithizonate and cadmium has been completely extracted from the solution.

4. The removal of the noble metals and copper from solution by precipitation with a suitable reducing agent (hydroxylamine hydrochloride, hypophosphorous acid) is not admissible because the precipitated metals carry down cadmium.

5. By using the glass-stoppered comparison tubes described on p. 42 and extracting with a small volume of dithizone, much less than 1  $\gamma$  of cadmium can be determined (cf. p. 175). With 1 ml. of carbon tetrachloride, 0.03  $\gamma$  cadmium can then be detected.

### B. THE SULFIDE METHOD

This method is based on the formation of a colloidal suspension of cadmium sulfide. It is inferior to the dithizoné method in sensitivity and specificity. If the suspensions are compared in ultraviolet radiation from a mercury arc instead of in daylight, the sensitivity is increased ten-fold.<sup>4</sup> Juza and Langheim<sup>5</sup> use gelatin to stabilize the suspension, and make the determination photometrically. They find that Beer's law holds. In the presence of cyanide, 10 times as much copper and cobalt, 100 times as much nickel, and 1000 times as much zinc as cadmium may be present.

## III. Applications of the Dithizone Method

### A. SILICATE ROCKS<sup>6</sup>

The rock sample is decomposed with hydrofluoric-perchloric acid and the ammoniacal citrate solution of the residue is extracted with dithizone in carbon tetrachloride to isolate cadmium, zinc, lead, copper, etc. The carbon tetrachloride solution is shaken with very dilute hydrochloric acid to transfer cadmium, zinc, etc. to the aqueous phase; copper and cobalt remain in the carbon tetrachloride. Cadmium can then be determined in the aqueous phase after making strongly basic with sodium hydroxide.

The cadmium content of igneous rocks is of the order of  $10^{-5}$  per cent. The method described permits the detection of  $5 \times 10^{-6}$  per cent of cadmium when a 0.5 g. sample is taken. The only metal likely to give trouble is nickel. If the sample contains more than 0.03–0.04 per cent of nickel, some of this metal will find its way into the final solution and impart a brownish color to the carbon tetrachloride solution.

Because of the nature of the sample the concentrations of the reagents used here are different from those in the preceding general procedure. Although the directions call for comparison by the standard series method, a photometer can be used to determine the transmittancy (520  $m\mu$ ) if a suitable cell is available.

<sup>4</sup> L. T. Fairhall and L. Prodan, *J. Am. Chem. Soc.*, **53**, 1321 (1931).

<sup>5</sup> R. Juza and R. Langheim, *Angew. Chem.*, **50**, 255 (1937).

<sup>6</sup> E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **11**, 364 (1939).

### Special Reagents

*Dithizone*, 0.02 per cent (weight by volume) in carbon tetrachloride.

*Dithizone*, 0.001 per cent (weight by volume) in carbon tetrachloride. One milliliter of this solution shaken with 10 ml. of redistilled water and 2 to 3 ml. of 25 per cent sodium hydroxide solution should yield a colorless carbon tetrachloride layer. This solution should be prepared shortly before use by diluting the stronger dithizone solution.

*Sodium citrate*, 10 per cent. The solution should be freed from heavy metals by adding a few drops of concentrated ammonium hydroxide to 100 ml. and shaking with successive small portions of 0.01 or 0.02 per cent dithizone in carbon tetrachloride until the latter shows only a very faint pink color.

*Sodium hydroxide*, 25 grams in 100 ml. of solution.

*Hydrochloric acid*, approximately 0.01 *N*. Dilute 1 volume of concentrated acid with 1000 of redistilled water. The solution should be shaken with a few milliliters of 0.01 per cent dithizone in carbon tetrachloride and decanted from the latter before use.

### ¶ Procedure

Weigh 0.5 gram of rock powder into a platinum dish and add a few milliliters of water, 1 ml. of 70 per cent perchloric acid, and 5 ml. of hydrofluoric acid. Evaporate to dryness, add 0.5 ml. of perchloric acid and a few milliliters of water to the residue, and again evaporate to dryness to expel excess perchloric acid. Moisten the residue with 1 ml. of concentrated hydrochloric acid, add 5 ml. of water, and heat near the boiling point until all soluble matter has been brought into solution.

Add 10 ml. of sodium citrate solution and 0.1 gram of hydroxylamine hydrochloride, neutralize with concentrated ammonium hydroxide using litmus paper, and add 2 drops in excess. If the solution is appreciably turbid at this point, filter through a small filter paper, wash with small portions of water, and ash the paper at a low temperature. Grind the residue with 0.15 to 0.2 gram of sodium carbonate in an agate mortar, transfer the powder to a platinum crucible, and fuse. Leach the melt with water, filter through paper, wash with a few milliliters of water, rinse the insoluble material out of the paper, and heat with dilute hydrochloric acid to effect as complete solution as possible. Add 2 or 3 ml. of sodium citrate and a small crystal of hydroxylamine hydrochloride, neutralize with ammonium hydroxide, and add 2 drops in excess.

Extract the main solution (filtrate from any insoluble material) as follows: Add 5 ml. of 0.02 per cent dithizone and shake in a separatory funnel for 0.5 to 1 minute; allow the carbon tetrachloride to settle and draw it off into another separatory funnel. If the carbon tetrachloride drawn off is not greenish, add 2 to 3 ml. more of dithizone to the main solution, shake, draw off, and repeat until the carbon tetrachloride layer shows a greenish color after shaking for 1 minute. In like manner extract the solution re-

sulting from the sodium carbonate fusion, using 1-ml. portions of dithizone in this case.

Combine all the dithizone extracts and shake with 5 ml. of water; discard the water layer. Shake the carbon tetrachloride extract vigorously with 5 ml. of 0.01 *N* hydrochloric acid for 2 minutes. Draw off the carbon tetrachloride layer and repeat the shaking with a fresh 5-ml. portion of 0.01 *N* hydrochloric acid. Combine the acid extracts and discard the carbon tetrachloride. Shake the hydrochloric acid extract with small portions of carbon tetrachloride to remove any colored droplets of carbon tetrachloride in the solution. Finally all droplets of carbon tetrachloride should be separated from the aqueous layer; care should be taken that a film of tetrachloride does not remain on the water surface. The loss of a drop or two of aqueous phase in removing carbon tetrachloride will do no harm.

Transfer the solution to a flat-bottomed glass-stoppered tube,  $1.8 \times 15$  cm., and rinse the separatory funnel with a milliliter or two of water. Prepare a series of standards in similar tubes containing, for example, 0, 0.05, 0.1, 0.15 . . . microgram of cadmium, dilute with 0.01 *N* hydrochloric acid to the same volume as the unknown, and mix. Add 2.5 ml. of 25 per cent sodium hydroxide solution to each tube and mix. Then add 1.0 ml. of 0.001 per cent dithizone solution and shake vigorously 10 to 15 times. Compare the colors of the carbon tetrachloride layers by viewing the tubes transversely against a white background. The colors fade on standing, and the hue also changes, so that the color comparison should be made immediately after shaking. The hue of the unknown should be the same as that of the standards.

Run a blank on the reagents, taking double the amounts used in the determination itself.

**Notes.**—1. Hydroxylamine hydrochloride is added to prevent air-oxidation of manganese to higher valences; such oxidation results in incomplete extraction of cadmium.

2. The excess of ammonia added prior to the dithizone extraction of the sample must not be too great, otherwise nickel is extracted in large amounts and later gives rise to difficulties in the color comparison.

3. The accuracy of the method may be judged from the following figures:

Cd present 10 <sup>-6</sup> %	Cd found 10 <sup>-6</sup> %	
2	1.5	
4	5, 4.5	
7	6.5	
3	3	(0.04% Ni)
4	4.5	(0.02% Ni)
4	3	(0.01% Ni, 0.2% Mn)

## B. ZINC METAL

For the determination of less than 0.01 per cent of cadmium in zinc a preliminary concentration of cadmium by sulfide precipitation is necessary. The following procedure permits the determination of as little as 0.001-0.002 per cent cadmium with an accuracy of 5 to 10 per cent.

¶ Procedure<sup>7</sup>

Dissolve 25 g. of zinc in dilute nitric acid, neutralize the solution with ammonia, warm, and add a dilute solution of sodium sulfide with stirring to precipitate a portion of the zinc and all or most of the cadmium. The zinc sulfide first precipitated is generally discolored by small amounts of other heavy metals present, and the precipitation of cadmium may be considered complete when further addition of sodium sulfide produces a pure white precipitate of zinc sulfide.

Filter off the precipitate, dissolve it in dilute nitric acid, evaporate the solution to a small volume to get rid of hydrogen sulfide and most of the acid, and transfer to a volumetric flask. Dilute the solution to volume with water and take for analysis an aliquot representing 1 or 2 g. of sample. Shake the dilute acid solution (*ca.* 0.05 *N*) with dithizone to remove copper and silver. Then determine cadmium as described on p. 172.

<sup>7</sup> H. Fischer and G. Leopoldi, *Mikrochim. Acta*, **1**, 37 (1937).

## CHAPTER XII

### CALCIUM

#### I. Separations

Precipitation of calcium as oxalate is the most generally applicable method for its isolation. Magnesium oxalate is coprecipitated (or sometimes postprecipitated) with calcium oxalate and a double precipitation of the latter is likely to be required if magnesium preponderates over calcium. If magnesium greatly outweighs calcium, the oxalate separation becomes uncertain because of the difficulty of precipitating calcium completely.<sup>1</sup> It is then advisable to follow Hillebrand's method of precipitating calcium together with magnesium ammonium phosphate, dissolving the precipitate in sulfuric acid, and separating calcium as sulfate in alcoholic medium.<sup>2</sup> Fortunately in many materials (biological samples, water, etc.) the calcium-magnesium ratio is such that special attention need not be paid to the effect of magnesium.

If the precipitation of calcium oxalate is carried out at a pH of 3 to 4, instead of in a slightly ammoniacal medium as is usually done, separation of calcium from iron, titanium, etc. as well as from much phosphate can be effected.<sup>3</sup> It may be calculated that the solubility of calcium oxalate in 0.1 *M* oxalate solution having a pH of 4 is less than 0.1 mg. Ca per liter.

For the separation of calcium from strontium, resort must be made to the extraction of the anhydrous nitrates with such solvents as absolute alcohol and ether, acetone,<sup>4</sup> or nitric acid (density 1.42), which dissolve calcium nitrate and leave most of the strontium (and barium) nitrate. This procedure has been applied particularly for the separation of little strontium from much calcium and there is little information available on its performance in the isolation of little calcium from much strontium. Barium is quite readily separated from calcium by precipitation as the chromate (p. 149).

<sup>1</sup> See I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*. Macmillan, New York, 1936; p. 333 for a discussion of the oxalate method for the separation of calcium and magnesium.

<sup>2</sup> W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*. Wiley, New York, 1929; p. 488.

<sup>3</sup> J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **20**, 607 (1938).

<sup>4</sup> According to M. M. Tillu and M. S. Telang, *J. Indian Chem. Soc.*, **19**, 231 (1942), the solubility of strontium nitrate in acetone is 1 part in 15,000 at 35° C.

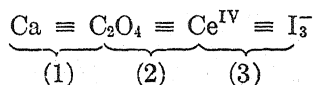


## II. Methods of Determination

Calcium must be determined by indirect colorimetric methods by making use of the reactivity of the anion of a slightly soluble calcium salt. Because of their indirect character the colorimetric methods for calcium are far from ideal, but nevertheless are useful for certain types of material, especially biological samples, in which the proportion of calcium is not too low. The two methods which have found the most favor are based on the precipitation of calcium as oxalate and phosphate respectively.

### A. THE OXALATE METHOD

Because of its low solubility, calcium oxalate recommends itself as the basis of a colorimetric method for calcium, especially since small amounts of magnesium will not interfere appreciably. Oxalate does not form colored compounds, but it readily reduces colored substances or those that can be made to yield strongly colored products. Ceric salts are probably best suited for the determination of calcium by the oxalate method. Solutions of ceric salts are not sufficiently intensely colored to permit their concentration to be determined advantageously in this way for the present purpose, but it is a simple matter to add iodide and obtain a strong-colored solution of tri-iodide ion. This is the method used by Sendroy for the micro and ultramicro determination of calcium.<sup>5</sup> It will be noted that the method is very much an indirect one:



The most crucial step in the sequence is (1), *i.e.*, all the calcium must be precipitated, no appreciable amount of calcium oxalate must be lost in washing, and the precipitate must contain calcium and oxalate in a 1:1 ratio (if the standard curve is based on known quantities of a soluble oxalate such as sodium oxalate). If these conditions can be fulfilled, the other steps should give little trouble, although in step (3) air-oxidation of the acid iodide solution may introduce error unless suitable precautions are taken.

So far as the requirements of the colorimetric method are concerned, the calcium oxalate precipitate formed in a slightly acid solution may be considered to have the theoretical ratio of calcium-oxalate, although actually it contains a little excess oxalate (coprecipitated ammonium oxalate or oxalic acid); a precipitate formed in an initially ammoniacal solution will contain a little less oxalate than it should (the ratio  $\text{Ca}/\text{C}_2\text{O}_4$  is of the order

<sup>5</sup> J. Sendroy, Jr., *J. Biol. Chem.*, **144**, 243 (1942).

1.01). Sodium is fairly strongly coprecipitated with calcium oxalate and leads to slightly high results (*ca.* 1 per cent), if present in high concentrations. The effect of magnesium may be more serious, and the error may be positive or negative depending on its amount as already indicated. Sulfate in sufficient concentration gives rise to low results owing to the coprecipitation of calcium sulfate. Phosphate is not coprecipitated with calcium oxalate to any serious extent if the precipitation of the latter is made in a medium initially slightly acid.

The following procedure is essentially the same as that given by Sendroy (*loc. cit.*) for the determination of calcium in blood serum. The error should not exceed  $\pm 2$  per cent.

### Reagents

*Ammonium oxalate solution*, saturated (4.5 per cent) at room temperature.

*Ammonium hydroxide*, 6 *N*.

*Washing mixture*. Mix equal volumes of water, absolute alcohol (or redistilled 95 per cent alcohol) and reagent-grade ethyl ether. This mixture on evaporation must not give a residue that reduces acid ceric solution.

*Sulfuric acid*, 1 *N*.

*Ceric sulfate ca. 0.1 N*. Dissolve 29 g. of anhydrous  $\text{Ce}(\text{HSO}_4)_4$  of 92 per cent purity or the equivalent weight of  $\text{Ce}(\text{SO}_4)_2$  in 500 ml. of 1 *N* sulfuric acid. The concentration of the solution should not differ too much from 0.1 *N*. Its strength may be checked by adding a suitable amount of the diluted solution to acidified potassium iodide solution and measuring the transmittancy (*cf.* p. 181). The calculated amount of water or ceric sulfate may then be added to make the solution more nearly 0.1 *N*.

*Ceric sulfate, 0.005 N in 0.2 N sulfuric acid*. Prepare from the 0.1 *N* ceric solution shortly before use.

*Sodium oxalate, 0.1000 N*. Dissolve 3.350 g.  $\text{Na}_2\text{C}_2\text{O}_4$  in water, add 50 ml. of 1 *N* sulfuric acid and dilute to 500 ml. Protect the solution from the light. It should be stable for 6 months.

*Sodium oxalate, 0.0025 N*. Prepare fresh from the 0.1 *N* solution by dilution with water.

*Potassium iodide*, 1 per cent. Prepare immediately before use by dissolving 1.0 g. of analytical quality salt in 100 ml. of water.

*Potassium iodate, 0.0005 M*. Prepare from pure dry  $\text{KIO}_3$ , accurately weighed. This solution is used to furnish iodine by reaction with an acidified iodide solution, for the construction of the calibration curve.

### ¶ Procedure

The following directions may be used for the determination of 0.05–0.15 mg. of calcium (for smaller amounts see Note 1) in the absence of such interfering substances as have been mentioned above.

To the neutral sample solution in a 10 to 15 ml. Pyrex conical bottomed centrifuge tube<sup>6</sup> add sufficient water to make the volume 5 ml., 1 or 2 drops

<sup>6</sup> Instead of employing the centrifuge technique, one can as well work with the filter stick, using the apparatus illustrated on p. 367.

of concentrated hydrochloric acid, 1 ml. of saturated ammonium oxalate solution, and then enough dilute ammonia to make the liquid basic to methyl orange ( $pH$  4.5 or above). In the same manner treat two "standard" tubes containing 5 ml. of water. Allow the solutions to stand overnight.

Centrifuge each tube for 5 minutes, and by means of a capillary with an upturned tip draw off all but about 0.2 ml. of the supernatant liquid. Wash the entire inside of the tube with 3 ml. of water added from a pipet moved around the top of the tube. Mix the water with the residual solution by tapping the tube until the precipitate just starts to rise. Then centrifuge and withdraw the liquid as before. Next wash with the water-alcohol-ether mixture as follows. Add 1 ml. of the mixture, stir to mix well, add an additional 3 ml. and mix gently with the first 1 ml. portion so as not to bring much of the precipitate into the supernatant layer. Centrifuge and draw off the supernatant liquid. Repeat the washing and withdrawal. Dry the tubes for  $\frac{1}{2}$  to 1 hour in an oven at  $100-110^\circ$ , inclining them at an angle of  $15^\circ$ .

At this point add 1.00 and 3.00 ml. of 0.0025  $N$  sodium oxalate solution to the two standard tubes. Then add 2.0 ml. of 0.5  $N$  sulfuric acid to all the tubes, and heat the latter for 5 minutes in a beaker of water kept below the boiling point. Cool to room temperature, add 2.00 ml. of 0.005  $N$  ceric solution, mix and allow the covered tubes to stand for 30 minutes at room temperature, or alternatively in a water bath at  $70^\circ$  for 10 minutes.

Transfer the solutions to a 25 ml. volumetric flask and dilute to about 20 ml. Add 1.5 ml. of 1 per cent potassium iodide solution, mix, dilute to volume and mix again. Without undue delay determine the transmittancy of the solutions with the aid of a filter showing maximum transmission at  $400\text{ m}\mu$ , against a reagent blank containing the same concentration of sulfuric acid and potassium iodide as the sample and standard solutions, and which has been prepared at the same time as these. Error due to liberation of iodine by air-oxidation will be cancelled out by the use of such a solution as a reference liquid representing 100 per cent transmittancy.

The concentration of calcium in the *diluted* sample is equal to

$$\frac{[C_2O_4^-]_{s_1} + [C_2O_4^-]_{s_2} + [I_2]_{s_1} + [I_2]_{s_2}}{2} - [I_2]_u,$$

where the brackets denote equivalent concentrations at the volume of dilution (25 ml.) and the subscripts  $s_1, s_2$  and  $u$  refer to the standards and the sample solution.

Construct the iodine calibration curve by mixing from 1 to 10 ml. of 0.0005  $M$  potassium iodate solution with 10 ml. of 0.5  $N$  sulfuric acid and 6 ml. of 1 per cent potassium iodide solution, and diluting to 100 ml. with

water in a volumetric flask; obtain the transmittancy, using a similar sulfuric acid-iodide solution prepared at the same time for reference (= 100 per cent transmission). Plot extinction versus iodine concentration.

**Notes.**—1. By appropriately reducing the volume and concentration of the solutions used, quantities of calcium much smaller than 0.1 mg. can be determined. Reference must be made to the paper of Sendroy, cited above, for details. When very small quantities of calcium are involved, it may be advantageous to augment the color of iodine-iodide solutions by the addition of ethyl alcohol. Moreover, starch suspension can be added to the iodine solution and the transmittancy of the blue solution determined by the use of a suitable filter, although the blue color is less stable than the yellow of  $I_2^-$  and more subject to variation from the effect of such factors as temperature.

2. The dilute (0.005 *N*) ceric sulfate solution is not stable for more than a few hours, but no error as the result of its decomposition is introduced when oxalate standards are used.

### B. THE PHOSPHATE METHOD<sup>7</sup>

This method involves the precipitation of tri-calcium phosphate, solution of the washed precipitate in acid, and the determination of phosphate in the solution by the molybdenum blue method. The procedure described on p. 141 involving the use of hydrazine sulfate as reducing agent for arsenic may also be applied to the determination of phosphate. Alternatively an aminonaphthol sulfonic acid-sulfite reagent may be used for the reduction of phosphomolybdate to molybdenum blue. The procedure given below utilizes this reagent.

#### Reagents

*Ammonium oxalate*, 4 g. of the monohydrate in 100 ml. of water.

*Sodium hydroxide*, 6 *N*. Prepare by diluting 18 *N* carbonate-free sodium hydroxide; keep the solution in a paraffin-lined vessel. Obtain the 18 *N* sodium hydroxide by dissolving 500 g. of the C.P. solid in 450 ml. of water with cooling, allowing the suspended sodium carbonate (which is practically insoluble in the solution) to settle, and then filtering or drawing off the clear supernatant liquid; the latter must be kept in a paraffin-coated bottle protected from the carbon dioxide of the air.

*Tri-sodium phosphate*, 1 per cent aqueous solution.

*Alcoholic wash solution*. Mix 58 ml. of ethyl alcohol with 10 ml. of amyl alcohol and dilute to 100 ml. with water. Add 1 drop of 6 *N* sodium hydroxide to make the solution neutral or very slightly basic.

*Ammonium molybdate*, 2.5 per cent in 6 *N* sulfuric acid.

*Aminonaphthol sulfonic acid reagent*. Dissolve 15 g. of sodium bisulfite and 0.5 g. of sodium sulfite in 100 ml. of water. Add 0.25 g. of 1-amino 2-naphthol 4-sulfonic acid and shake at intervals for a few hours. Filter the solution if it is not clear and keep it in a dark bottle. The solution should be made up fresh every 2-3 weeks.

*Standard phosphate solution*, 1.00 mg. P per ml. Dissolve 0.439 g. of pure dry

<sup>7</sup> A. B. Briggs, *J. Biol. Chem.*, **59**, 255 (1924); J. H. Roe and B. S. Kahn, *ibid.*, **81**, 1 (1929); T. Kuttner and H. R. Cohen, *ibid.*, **75**, 517 (1927).

$\text{KH}_2\text{PO}_4$  in water and dilute to 100 ml. This solution may be further diluted, as preferred, to give solutions containing 0.1 or 0.01 mg. P per ml.

### ¶ Procedure

The sample may conveniently contain 0.2–0.5 mg. of calcium.

Magnesium if present in more than mere traces necessitates the isolation of calcium as the oxalate. The following directions may be used for the separation of calcium from magnesium when the latter is not greatly preponderant, and metals such as iron, aluminum, strontium, etc., which are precipitated by ammonia or oxalate, are absent. To 5 or 10 ml. of the solution add a drop of methyl orange and several drops of hydrochloric acid in excess of that required to make the solution acid. Heat to near boiling, add 1 ml. of ammonium oxalate solution and then 1:1 ammonium hydroxide dropwise until the solution becomes yellow. Allow the solution to cool to room temperature with occasional stirring, and filter (or centrifuge) after 1 or 2 hours. Wash the precipitate with cold 0.1 per cent ammonium oxalate, dissolve it in a few drops of hot 1:1 hydrochloric acid, wash the filter with water, and evaporate the filtrate and washings to a volume of a few drops. Destroy the oxalate by adding 0.5 ml. of 30 per cent hydrogen peroxide and heating for one-half hour on the steam bath. Alternatively the calcium oxalate may be transformed into calcium carbonate by ignition at low redness and the latter dissolved in a drop or two of dilute hydrochloric acid.

Dilute the solution to 3 to 5 ml. with water and add 0.5 ml. of 6 *N* sodium hydroxide. Allow the solution to stand for a few minutes to permit the precipitation of any traces of magnesium present, and then add 0.5 ml. of trisodium phosphate solution. Let the solution stand for an hour to assure complete precipitation. Collect the precipitate by filtering (small porous porcelain or sintered glass crucible) or centrifuging, and wash carefully with the alcoholic mixture. Usually three 2 ml. portions of wash solution suffice. Allow most of the alcohol to evaporate and dissolve the precipitate in 0.5 ml. of the acid molybdate solution, wash with a little water if a filter was used, add 1 ml. of the aminonaphthol sulfonic acid reagent, and dilute to 10.0 ml. with water. Mix, allow to stand in the dark for 10 minutes and compare against a suitable phosphate standard prepared in a similar manner. For the most accurate results the standard phosphate solution should be obtained from a known amount of calcium treated in the same way as the sample.

### C. OTHER METHODS

Among other methods proposed for the colorimetric determination of calcium the following may be mentioned:

1. Precipitation as picrolonate,<sup>8</sup> solution of the precipitate in water and development of a red color by treatment with bromine and sodium hydroxide.
2. Precipitation as  $K_2CaNi(NO_2)_6$ <sup>9</sup> and determination of the nitrite in the precipitate.
3. Precipitation as tungstate<sup>10</sup> followed by determination of tungsten with titanous chloride.
4. Precipitation as 8-hydroxyquinolate<sup>11</sup> and determination of hydroxyquinoline in the precipitate with Folin's reagent.
5. Precipitation as alizarinate<sup>12</sup> followed by colorimetric determination of alizarin in the precipitate.

Calcium may be determined nephelometrically as a slightly soluble soap such as calcium oleate<sup>13</sup> or stearate, or as the oxalate.<sup>14</sup>

<sup>8</sup> F. Alten, H. Weiland, and E. Knippenberg, *Biochem. Z.*, **265**, 85 (1933). Cf. G. Cohn and I. M. Kolthoff, *J. Biol. Chem.*, **147**, 705 (1943).

<sup>9</sup> M. Mousseron, *Bull. soc. chim. biol.*, **12**, 1014 (1930); **13**, 831 (1931).

<sup>10</sup> M. Mousseron and N. Bouisson, *Bull. soc. chim. biol.*, **12**, 482 (1930).

<sup>11</sup> S. Yoshimatsu, *Tohoku J. Exptl. Med.*, **15**, 355 (1930).

<sup>12</sup> P. P. Laidlaw and W. W. Payne, *Biochem. J.*, **16**, 494 (1922).

<sup>13</sup> A. Gregoire, *J. Soc. Chem. Ind.*, **42**, 427A (1923); A. Gregoire, E. Carpiaux, E. Larose, and T. Sola, *Bull. soc. chim. Belg.*, **32**, 123 (1923).

<sup>14</sup> J. S. Sharpe, *Edinburgh Med. J.*, **33**, 27 (1926).

## CHAPTER XIII

### CERIUM

Cerium is distinguished from the other rare earth metals by its oxidizability in aqueous solution to the quadrivalent state, in which it shows a fairly strong yellow color (acid medium). It is thus possible to determine cerium directly in the presence of other rare earths as well as some of the common elements. The strong oxidizing character of ceric ion may be made the basis of an indirect colorimetric method by the formation of strongly colored oxidation products of various organic compounds. The indirect method gives promise of great sensitivity, but as yet it has not been developed as fully as might be desired.

#### I. Separations

Cerium (III) like the other rare earth metals forms an oxalate only slightly soluble in excess oxalic acid, and a fluoride very sparingly soluble in the presence of hydrofluoric acid. The latter precipitation form is generally considered the better one for the separation of cerium and the other rare earths from the metals of the ammonium hydroxide group. Calcium or strontium fluoride may perhaps be of value as collectors of cerous fluoride, but these precipitates are difficultly filterable (*cf.* p. 370). Lanthanum has an ionic radius very close to that of cerium (III) and may be expected to function well as a collector for cerous fluoride or oxalate.

At times precipitation of cerium as the extremely slightly soluble ceric hydroxide should be of value in separations (for example from  $\text{Cr}^{\text{VI}}$ ).

#### II. Methods of Determination

##### A. THE PERSULFATE METHOD (COLOR OF CERIC ION)

The color of quadrivalent cerium in acid medium is not as intense as might be desired, but it is strong enough to allow moderately small amounts of cerium to be determined. At room temperature in 1 *N* sulfuric acid solution the visual sensitivity is approximately 10  $\gamma$  Ce per square centimeter, and the photometric sensitivity (p. 40) with a blue filter is approximately 0.5  $\gamma$  Ce per square centimeter. No doubt the sensitivity can be considerably increased by employing monochromatic light in the violet portion of the spectrum.<sup>1</sup> The color intensity of ceric solutions increases slightly with a rise in temperature. Beer's law is followed.

<sup>1</sup> See C. T. Kasline and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **8**, 463 (1936), for the transmission curve of ceric sulfate above 480 m $\mu$ .

Cerous ion may conveniently be oxidized to ceric by ammonium persulfate in hot dilute sulfuric acid solution with silver ion as catalyst. Since chromium and manganese are also oxidized to strongly colored dichromate and permanganate under these conditions, no appreciable amounts of these metals may be present. Chloride, fluoride, and phosphate must be absent. The effect of ferric iron and other colored ions in small quantities can be compensated by using an aliquot of the sample solution, not oxidized with persulfate, in the reference cell of the photometer. Alternatively, a drop of hydrogen peroxide can be added to reduce ceric ion to colorless cerous ion and the increase in transmittancy found.

The following procedure has been found to give satisfactory results. Three solutions containing respectively 0.080, 0.080, and 0.40 mg. of cerium gave the respective values 0.080, 0.088 and  $0.40 \pm 0.02$  mg. by the standard series method ( $1.8 \times 15$  cm. tubes).

### ¶ Procedure

The volume of the solution should be as small as practicable. Chloride and other interfering substances mentioned above must be absent. Add sufficient sulfuric acid to the sample solution to make its concentration 1 to 2 *N*, 0.2 g. of ammonium persulfate (for a 10 ml. volume), and 0.5 mg. of silver nitrate. Boil gently for 5 minutes, cool, dilute to volume with water, and determine the transmittancy with a violet filter. The solutions for the construction of the standard curve should have the same sulfuric acid concentration as the sample and the transmittancies should all be determined at the same temperature.

### B. THE BRUCINE METHOD

Ceric ion in acid solution oxidizes various organic compounds such as brucine, sulfanilic acid,<sup>2</sup> benzidine,<sup>3</sup> morphine, etc. to fairly intensely colored products.<sup>4</sup> The reaction with brucine has been proposed for the determination of quadrivalent cerium.<sup>5</sup> A strong red color is produced when brucine is added to an acid ceric solution, but this fades in the course of a few seconds to an orange and finally a brownish color which is much less intense than the original. The color intensity becomes practically constant

<sup>2</sup> Sulfanilic acid has been used as a qualitative reagent for quadrivalent cerium by E. Montignie, *Bull. soc. chim.*, **6**, 889 (1939). A red color develops slowly in acid solution, reaches a maximum intensity and then fades. The sensitivity is less than with brucine. Arsanilic acid also gives an unstable red color (J. F. Miller, *Ind. Eng. Chem., Anal. Ed.*, **9**, 181 (1937)).

<sup>3</sup> R. G. Harry and E. A. Rudge, *J. Soc. Chem. Ind.*, **51**, 64T (1932).

<sup>4</sup> Very small quantities of cerium (IV) can probably be determined by the use of ferrous *o*-phenanthroline complex (diminution of the orange-red color).

<sup>5</sup> F. M. Shemyakin and V. A. Volkova, *J. Gen. Chem. U. S. S. R.*, **9**, 698 (1939).



in 5 or 10 minutes, but decreases on long standing.<sup>6</sup> The color of the oxidized brucine is 4 or 5 times as strong as the ceric solution producing it. The color intensity is proportional to the concentration of cerium.

Permanganate produces a yellow color, paler than that given by an equivalent amount of ceric ion. Chromate oxidizes brucine very slowly in acid solution, yielding a brown color. Ferric iron gives no appreciable coloration in small amounts. Persulfate slowly produces a yellow-brown color.

### ¶ Procedure

The solution may contain a few tenths of a milligram of cerium in a volume of about 10 ml., and should be approximately 1 *N* in sulfuric acid.

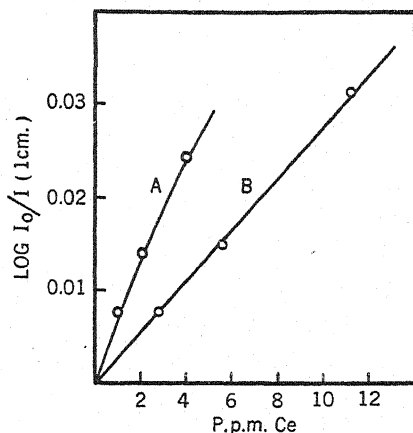


Fig. 26.—Determination of cerium by (A) the peroxide method (1 ml. 3% H<sub>2</sub>O and 5 g. K<sub>2</sub>CO<sub>3</sub> in a final volume of 25 ml.), and (B) as ceric sulfate in 1 *N* sulfuric acid solution; Wratten filter No. 47 used in both methods. (Data for the peroxide method obtained by R. A. Johnson, University of Minnesota.)

Oxidize cerous cerium with ammonium persulfate as described on p. 186, except boil for 10 minutes, adding water if necessary, to be certain that all persulfate is destroyed. Cool the solution to room temperature, add 0.25 ml. of 0.1 per cent brucine in 1 *N* sulfuric acid, and dilute to volume (10 ml. if possible). Determine the transmittancy of the solution after 10 minutes, using a blue filter. It is advisable to read the solution again after

<sup>6</sup> A solution of ceric sulfate containing 28 p.p.m. of Ce treated as described in the procedure showed the following extinctions after various times of standing: 5 minutes, 0.096; 10 minutes, 0.098; 20 minutes, 0.098; 1 hour, 0.092; 3 hours, 0.091. A solution containing 14 p.p.m. Ce showed practically the same reading after 1 hour as after 5 minutes.

another 10 minutes to be certain that the transmittancy is not changing as the result of the presence of undecomposed persulfate.

#### C. THE CARBONATE-PEROXIDE METHOD

A dilute solution of a cerous salt gives a white precipitate of the carbonate when treated with potassium carbonate, which dissolves in an excess of the latter. On standing, the solution becomes yellow owing to the formation of perceric carbonate by air-oxidation. This reaction has been made the basis of a colorimetric method.<sup>7</sup> The yellow color appears at once if hydrogen peroxide is added. Uranium gives a yellow or yellow-orange color under the same conditions.

<sup>7</sup> J. Plank, *Z. anal. Chem.*, **116**, 312 (1939).

## CHAPTER XIV

### CHROMIUM

#### I. Separations

The most useful method for the separation of chromium involves oxidation in basic medium, whereby chromate is formed and remains in solution while a great many metals such as iron, titanium, manganese, nickel, cobalt, etc. are precipitated. The elements remaining in solution with chromium are in part innocuous so far as the succeeding colorimetric determination is concerned (aluminum, arsenic, phosphorus), and in part disturbing (uranium in the chromate comparison method, vanadium and much molybdenum in the diphenylcarbazide method). The oxidation can be effected in hot solution with sodium peroxide or with hydrogen peroxide and sodium hydroxide. The oxidation can also be carried out by fusion with sodium peroxide, with a 10:1 mixture of sodium carbonate and potassium nitrate, or even sodium carbonate alone for some samples such as silicate rocks. Manganese is oxidized to manganate in the fusion but this can be reduced to hydrated manganese dioxide by adding alcohol to the hot solution of the melt. Chromium shows little tendency to be retained in the insoluble material remaining after leaching the sodium carbonate melt of a silicate, and a refusion is ordinarily not required. A flux containing too much nitrate or too high a temperature in the fusion should be avoided as possibly leading to an attack of the platinum crucible and introduction of a little platinum into the solution.

The slight solubility of chromic hydroxide enables chromium to be separated from most of the metals accompanying chromium in the above chromate separation; the chromate is reduced to the trivalent state and the boiling solution treated with an excess of sodium hydroxide. If carbonate is also added, uranium will remain in solution. Perhaps a very small amount of ferric iron can be added as collector; its amount should not exceed a few tenths of a milligram if chromium is to be determined by the diphenylcarbazide method which permits the presence of very little iron.

Vanadate can be separated from chromate by adding 8-hydroxyquinoline to the solution and extracting at a *pH* of about 4 with chloroform. Chromium is left in solution (p. 197). Vanadium as well as iron can be precipitated in acid solution with cupferron and thus separated from chromium (III).

Ether extraction of a hydrochloric acid solution separates most of the ferric iron as well as molybdenum (if iron is present in excess) from chro-

mium. Another method for removal of most of the iron involves precipitation of chromium with sodium bicarbonate from a solution containing iron in the ferrous state (p. 198).

## II. Methods of Determination

The diphenylcarbazide method for chromium is at least five times as sensitive as the chromate method,<sup>1</sup> and possesses the further advantage of giving a color not to be mistaken for that of any other substance. On the other hand the chromate method serves well when the quantity of chromium is not too small. It can be carried out very simply and is not affected by the presence of vanadium.

### A. THE CHROMATE METHOD

This method is generally applied after oxidation of chromium in basic solution or by alkaline fusion, which effects a simple separation from most of the cations giving colored solutions. Procedures for the oxidation have already been mentioned. So far as color intensity is concerned the determination could also be carried out in acid medium (oxidation with persulfate in the presence of silver as catalyst)<sup>2</sup> but then iron and other metals would interfere.

At low concentrations chromate solutions obey Beer's law closely (p. 61). Chromate ion absorbs strongly below  $480\text{ m}\mu$ , with maximum absorption at about  $370\text{ m}\mu$ . When a filter photometer is used in measuring the transmittancies of chromate solutions, the optical density may not be proportional to the chromium concentration because of the difficulty in obtaining a sufficiently selective filter, with the result that the measurement is made at the edge of the absorption band.

The most serious interference in the chromate method results from uranium and cerium which can pass into the filtrate, imparting a yellow color to it. Copper also may be found in the filtrate in small amounts giving rise to a faint blue color. Iron will at times be found in the filtrate in colloidal form. The yellow coloration thus resulting may be comparatively strong when the sample contains both much iron and silica. Alkaline solutions may extract from filter paper substances imparting a faint yellowish color to the filtrate.

<sup>1</sup> The respective spectrophotometric sensitivities correspond to 0.01 ( $366\text{ m}\mu$ ) and 0.002 ( $540\text{ m}\mu$ )  $\gamma$  Cr per  $\text{cm}^2$ . If the absorption of the chromate solution is measured at longer wave lengths the advantage of the carbazide method becomes relatively greater.

<sup>2</sup> For transmission curves of chromate and dichromate solutions see C. T. Kasline and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **8**, 463 (1936).

### ¶ General Procedure

Convert chromium in the sample to the sexivalent state by a suitable method (*cf.* p. 189) and dilute the clear alkaline solution to such volume that the chromium concentration is 5–100 p.p.m. Obtain the transmittancy of the solution with the aid of a filter having maximum transmission in the violet portion of the spectrum (370  $m\mu$  is the best wave-length). The standard solutions for the construction of the reference curve should have the same alkalinity as the sample solution and should preferably

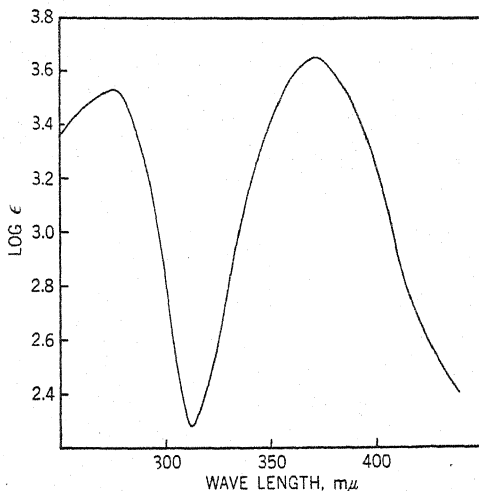


Fig. 27.—Absorption curve of potassium chromate in 0.05 *N* potassium hydroxide (after G. Rössler).

have the same concentration of foreign salts such as sodium carbonate. Standards may be prepared from potassium chromate  $\left(\frac{K_2CrO_4}{Cr} = 3.73, \frac{2 K_2CrO_4}{Cr_2O_3} = 2.55\right)$ .

If a Duboscq colorimeter is used, the chromium concentration of the solution may be in the neighborhood of 10 p.p.m. In the standard series method of comparison, solutions as dilute as 1 p.p.m. may be used in  $1.8 \times 15$  cm. tubes. The colorimetric titration technique may also be conveniently applied.

### B. THE DIPHENYLCARBAZIDE METHOD

In acid solution diphenylcarbazide gives a soluble red-violet product with sexivalent chromium.<sup>3</sup> The formula of the colored substance is not known.

<sup>3</sup> A. Cazeneuve, *Bull. soc. chim.*, [3] 23, 701 (1900); 25, 761 (1901).

The reaction is extraordinarily sensitive, the molar extinction coefficient of the colored compound, calculated on the basis of the molarity of the dichromate solution, being 31,400<sup>4</sup> at 540 m $\mu$ , the wave length of maximum absorption.

This reaction is the basis of the best method for the determination of the most minute amounts of chromium.<sup>5</sup> The method is nearly specific for chromium in the sense that the only element giving a similar violet color in mineral acid solution is molybdenum (VI), which however reacts much less sensitively. Mercury (I and II) gives a blue or violet-blue color, but except at low acidities the reaction is not sensitive. Iron (III) and vanadium (V) are disturbing elements, for they yield yellow or yellow-brown compounds with the reagent.

A suitable acidity for the chromium-diphenylcarbazide reaction is 0.2 *N*. At low acidities the color does not develop immediately, but in 0.2 *N* mineral acid solution maximum color intensity is attained within a few seconds. Sulfuric acid is to be preferred for acidification because iron gives less color in the presence of this acid than in the presence of hydrochloric acid. Solutions having an acidity much greater than 0.2 *N* are not desirable because the color is less stable in these. In 0.2 *N* sulfuric acid the chromium-diphenylcarbazide compound is quite stable<sup>6</sup> (see Table 22). Beer's law is closely followed, as several workers have found (Fig. 28). Reasonable amounts of neutral salts are without effect on the color; a solution 5 per cent in sodium sulfate showed the same color intensity as a salt-free solution.

The determination of chromium may be carried out in the presence of a limited amount of iron. As already mentioned, iron yields a yellow or brown color with diphenylcarbazide. Such a solution absorbs very little light above a wavelength of 460 m $\mu$ , and it has been stated<sup>4</sup> that the interference of iron can be eliminated by the use of a suitable green filter. If a sufficiently selective green filter is not used the error may be considerable (Table 22), especially if chloride is present. In sulfuric acid solution, with chloride absent, the yellow color developed by iron is not strong and good results can be obtained if the transmittancy of the solution is measured immediately after the addition of reagent. On standing the transmittancy of the solution increases. In the presence of phosphoric acid the transmittancy decreases on standing, but approximately correct results are

<sup>4</sup> G. P. Rowland, Jr., *Ind. Eng. Chem., Anal. Ed.*, **11**, 442 (1939).

<sup>5</sup> First used by A. Moulin, *Bull. soc. chim.*, **31**, 295 (1904).

<sup>6</sup> Rowland, *loc. cit.*, found the color to fade less rapidly than indicated by our figures. Thus a solution containing 0.375 p.p.m. Cr in ca. 0.1 *M* sulfuric acid gave the following values for  $I_0/I$ : 59.8 immediately after mixing, 60.1 after one-half hour, and 63.0 after 15 hours. Rowland used 1 ml. of alcohol saturated with the reagent for each 100 ml. of dichromate solution.

obtained on immediate reading. Practically, the presence of iron in the sample is a matter of little concern since it is usually separated in the oxidation of the chromium.

The interference of vanadium is a more serious possibility because it gives a stronger yellow color than does iron and it is not separated in the preparation of the sample for analysis. If the ratio of vanadium to chromium does not exceed 10:1, nearly correct results for chromium can be obtained by allowing the solution to stand for about 10 minutes after the addition of the reagent. The vanadium-diphenylcarbazide color fades fairly rapidly so that the nearly pure red-violet chromium color is obtained after 10–15 minutes if the vanadium is not too greatly preponderant. When the ratio is unfavorable, vanadium must be separated. This may be done conveniently by adding 8-hydroxyquinoline to the solution and extracting

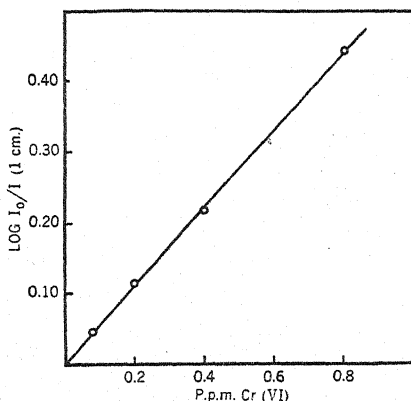


Fig. 28.—Determination of chromium (VI) with diphenylcarbazide (green filter, Cenco No. 2).

the compound  $V_2O_5(C_9H_6ON)_4$  at a pH of about 4 with chloroform.<sup>7</sup> The excess of the 8-hydroxyquinoline is simultaneously extracted by the chloroform, and chromate is left in the aqueous phase unchanged.<sup>8</sup>

Under the conditions recommended there is no interference from small amounts of mercury and molybdenum (Table 22).

#### Reagents

*Diphenylcarbazide*, 0.25 per cent in a 1:1 mixture of acetone and water. Alternatively a 0.25 per cent solution in alcohol may be used. The solution becomes brown on standing and is preferably prepared fresh daily.

*Sulfuric acid*, 6 N, free from reducing substances. Add dilute potassium permanganate solution to the hot acid until a very faint pink color appears.

<sup>7</sup> E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 336 (1936).

<sup>8</sup> By applying the procedure described on p. 197, two solutions of 20 ml. containing 1.00 and 2.50  $\gamma$  of Cr in the presence of 300 and 200  $\gamma$  of V respectively yielded the values 1.03 and 2.52  $\gamma$  of Cr. A filter photometer was used.

TABLE 22

## DETERMINATION OF CHROMIUM BY THE DIPHENYLCARBAZIDE METHOD

The sample solution was 0.2 *N* in sulfuric acid and contained 1 ml. of 0.25 per cent diphenylcarbazide solution (in 50 per cent acetone) per 25 ml. A filter photometer was used with a green filter (Cenco No. 2).

Addition	Cr taken p.p.m.	Cr found p.p.m.	Remarks
	0.800	(Stand- ard)	
	0.800	0.800	2 ml. diphenylcarbazide
	0.405	0.409	
	0.405	0.410	0.5 <i>N</i> H <sub>2</sub> SO <sub>4</sub>
	0.405	0.413	2 minutes after mixing
		0.410	10 minutes after mixing
		0.403	20 minutes after mixing
		0.388	2 hours after mixing
	0.405	0.392	2 minutes after mixing
		0.392	10 minutes after mixing
		0.388	30 minutes after mixing
	0.20	0.21	
	0.080	0.084	
	0.080	0.078	2 minutes after mixing
		0.078	15 minutes after mixing
Mo <sup>VI</sup> , 200 p.p.m.	0.405	0.409	2 minutes after mixing
		0.402	10 minutes after mixing
Hg <sup>II</sup> , 200 p.p.m. (as Hg(Cl <sub>2</sub> ))	0.405	0.405	
Fe <sup>III</sup> (as FeCl <sub>3</sub> ), 200 p.p.m.	0.405	0.51	2 minutes after mixing
		0.46	5 minutes after mixing
		0.445	10 minutes after mixing
Fe <sup>III</sup> (as FeCl <sub>3</sub> ), 100 p.p.m.	0.405	0.47	2 minutes after mixing
		0.46	5 minutes after mixing
		0.44	10 minutes after mixing
Fe <sup>III</sup> (as ferric alum), 200 p.p.m.	0.405	0.413	2 minutes after mixing
		0.385	5 minutes after mixing
		0.37	10 minutes after mixing
Fe <sup>III</sup> (as ferric alum), 200 p.p.m.	0.200	0.24	2 minutes after mixing
Fe <sup>III</sup> (as ferric alum), 200 p.p.m. (solution contained 1 ml. of 1:5 H <sub>3</sub> PO <sub>4</sub> in addition to sulfuric acid).	0.405	0.409	2 minutes after mixing
		0.425	5 minutes after mixing
		0.45	15 minutes after mixing
Fe <sup>III</sup> (as ferric alum), 200 p.p.m. (solution contained 1 ml. of 1:5 H <sub>3</sub> PO <sub>4</sub> in addition to sulfuric acid).	0.080	0.089	3 minutes after mixing
		0.11	7 minutes after mixing
V <sup>V</sup> , 4 p.p.m.	0.405	0.44	2 minutes after mixing
		0.425	5 minutes after mixing
V <sup>V</sup> , 4 p.p.m. (solution contained 1 ml. 1:5 H <sub>3</sub> PO <sub>4</sub> in addition to sulfuric acid).	0.080	0.104	2 minutes after mixing
		0.088	20 minutes after mixing



### ¶ Procedure

The sample solution may contain from 0.02 to 0.5 p.p.m. of Cr (VI). To 10–20 ml. of solution add sufficient sulfuric acid to make its concentration approximately 0.2 *N* when diluted to 25 ml., mix, add 1 ml. of diphenylcarbazide solution, and make up to 25 ml. with water. Determine the transmittancy of the solution soon after the addition of the reagent unless vanadium is present in appreciable amounts (the solution then is red or brownish instead of red-violet) in which case read after 10 to 15 minutes to obtain more nearly correct results. Use a green filter having the transmission maximum at 540  $m\mu$ .

When a Duboscq colorimeter is used, a suitable chromium concentration is 0.5 p.p.m.

### C. OTHER METHODS

Disodium-1,8-dihydroxynaphthalene-3,6-disulfonate (chromotropic salt) reacts with chromium (VI) in acid solution to give a soluble compound of red color.<sup>9</sup> The reagent has been used for determining chromium in steel<sup>10</sup> and in plant ash.<sup>9</sup> The reaction is sensitive. Ferric iron gives a green color (not formed in the presence of sufficient phosphoric acid), vanadium (V) a brown color, and titanium a red or red-brown color, all in acid solution.

Serichrome Blue R also has been used for the colorimetric determination of chromium by "after chroming" of wool dyed by it.<sup>11</sup>

## III. Applications of the Chromate and Diphenylcarbazide Methods

### A. SILICATE ROCKS

The chromate method may be used for samples containing fair amounts of chromium, say more than 0.01 per cent  $Cr_2O_3$ . The accurate determination of smaller amounts of chromium requires the use of the diphenylcarbazide method.

### ¶ Procedure for Chromate Method

Fuse 1 or 2 g. of very finely ground rock powder with five times its weight of a 10:1 mixture of sodium carbonate and sodium nitrate until complete decomposition has been effected. Leach the melt with 25–50 ml. of water. The cake should be transferred to a small beaker and disintegrated with a

<sup>9</sup> P. Koenig, *Chem. Ztg.*, **35**, 277 (1911).

<sup>10</sup> F. Garrat, *J. Ind. Eng. Chem.*, **5**, 298 (1913).

<sup>11</sup> G. C. Spencer, *Ind. Eng. Chem., Anal. Ed.*, **4**, 245 (1932).

glass rod flattened at one end. Add a few drops of alcohol and heat near the boiling point until all manganate has been reduced. Filter through paper previously washed with a little hot sodium carbonate solution, and wash the precipitate with hot water containing a little sodium carbonate. Collect the filtrate in a suitable color comparison tube (or volumetric flask if the color is strong) and compare against a standard chromate solution containing sodium carbonate. If the color is very faint it may not be due to chromium (p. 190) and the diphenylcarbazide method should be applied as described below.

#### ¶ Procedure for Diphenylcarbazide Method

The exact procedure to be followed depends upon the vanadium content of the rock sample. If vanadium does not greatly preponderate over chromium ( $V < 10 \text{ Cr}$ ), the latter can usually be determined directly, but with unfavorable vanadium-chromium ratios a separation of vanadium by 8-hydroxyquinoline is required.

**1. Direct Determination of Chromium.**—Mix 0.25 to 0.5 g. of finely ground sample (0.0001 to 0.1 per cent Cr) with five times its weight of sodium carbonate,<sup>12</sup> and fuse in a platinum crucible for 15 or 20 minutes in the usual case but longer if magnetite, ilmenite, etc. are present in appreciable amounts. (If the amount of vanadium in the sample is unknown it is advisable to fuse a larger sample so that an aliquot can be treated for the removal of vanadium if this is found to interfere in the direct determination of chromium.) Leach the melt with hot water, preferably by transferring the cake to a small beaker and triturating with a glass rod flattened at one end. Restrict the volume of water to about 5 ml. if the solution is finally to be made up to 25 ml. Add a few drops of alcohol and heat near the boiling point until all manganate has been reduced.

Filter through a very small filter paper into a 25 or 50 ml. volumetric flask. Wash with hot water containing a little sodium carbonate. Cool the combined filtrate and washings and carefully add dilute sulfuric acid to neutralize the sodium carbonate and make the acidity approximately 0.2 *N* when the solution has been diluted to volume (1.0 g.  $\text{Na}_2\text{CO}_3$  requires 3.2 ml. of 6 *N* sulfuric acid for neutralization). Swirl the solution carefully to liberate carbon dioxide in supersaturated solution, add 1 or 2 ml. of 0.25 per cent diphenylcarbazide solution, and make up to 25 or 50 ml. with water. Mix and obtain the transmittancy of the solution, or com-

<sup>12</sup> Sodium carbonate will not completely decompose chromite, and if this mineral is likely to be present sodium carbonate-nitrate or sodium peroxide must be used. The diphenylcarbazide method, however, is not likely to be applied when chromite is present, for this will generally mean a sample relatively high in chromium. If nitrate or peroxide is used in the fusion, the acidified filtrate must be treated with persulfate (p. 198) to reoxidize chromium.

pare against a standard solution in a Duboscq colorimeter (p. 195). If the sample solution is red or red-brown, vanadium exceeds chromium in amount. In such a case better results are obtained if the transmittancy is determined after 10–15 minutes, when the vanadium color will have been considerably reduced through fading.

**2. Determination of Chromium after Separation of Vanadium with 8-Hydroxyquinoline.**—Fuse the sample and leach the melt as described under (1). Dilute the filtrate and washings to volume and transfer an aliquot representing 0.1 to 0.25 g. of sample to a small separatory funnel. From a buret add exactly the volume of 2 *N* sulfuric acid required to neutralize the solution, as found by adding methyl orange to another aliquot and titrating with the acid until the color of the indicator just deviates from pure yellow.<sup>13</sup> Swirl the solution to liberate excess carbon dioxide. Add 0.1 ml. of 2.5 per

TABLE 23  
DETERMINATION OF CHROMIUM IN VARIOUS MATERIALS  
BY THE DIPHENYLCARBAZIDE METHOD

Sample	Cr present <sup>a</sup> %	Cr found %	Remarks
1. Silicate rock.....	0.0018	0.0017	
2. Silicate rock (0.10% V <sub>2</sub> O <sub>5</sub> ).....	0.0048	0.0044	Vanadium separated with 8-hydroxyquinoline
3. Silicate rock (0.10% V <sub>2</sub> O <sub>5</sub> ).....	0.035	0.034	Vanadium separated with 8-hydroxyquinoline
4. Peat ash.....	0.0075	0.0071	

<sup>a</sup> Most of chromium present was added; samples originally contained following percentages of Cr: (1) 0.0004 (2) 0.0014 (3) 0.0014 (4) 0.0025.

cent 8-hydroxyquinoline solution in 2 *N* acetic acid (sufficient for 0.2–0.3 mg. V) and extract with two 3 ml. portions of pure chloroform, shaking  $\frac{1}{2}$ –1 minute each time. Discard the chloroform. Add another 0.1 ml. portion of 8-hydroxyquinoline solution and shake with two more 3 ml. portions of chloroform. The last chloroform extract should be virtually colorless. To remove chloroform droplets from the solution, filter through a very small filter paper previously washed with water and catch the filtrate in a 25 or 50 ml. volumetric flask. Wash the separatory funnel and filter with a few small portions of water. Make the filtrate and washings about 0.2 *N* in sulfuric acid and add 1 ml. of 0.25 per cent diphenylcarbazide solution. Dilute the solution to volume and obtain the transmittancy.

<sup>13</sup> Methyl orange may be added to the solution used in the analysis if the latter is boiled with ammonium persulfate-silver nitrate after the removal of vanadium, the indicator then being destroyed.

**Note.**—With pure reagents there is no reduction of sexivalent chromium in the above procedure, but if desired the solution may be oxidized with persulfate to assure the presence of all the chromium as chromate. After the extraction of vanadium, make the solution about 0.5 *N* in sulfuric acid, add 1.0 ml. of 1 per cent silver nitrate and 0.5 g. of ammonium persulfate for each 25 ml. of solution, and boil for 10 minutes. Cool, filter to remove any precipitate of silver chloride, add 1 or 2 ml. of diphenylcarbazide solution, and make up to 25 or 50 ml.

## B. IRON ORE

### ¶ Procedure

Mix 0.5 g. of sample with 5 g. of sodium peroxide in a nickel or iron crucible, free from chromium, and heat carefully until the mixture is completely fused. Leach the melt with water, transfer the solution and insoluble matter to a volumetric flask (50 to 250 ml. depending on the amount of chromate), make up to the mark, and mix. Filter through dry asbestos. If the color of the filtrate is sufficiently strong, compare against a standard potassium chromate solution. Otherwise, take a suitable aliquot of the filtrate (say 25 or 50 ml.), and boil the solution for a few minutes to decompose most of the peroxide. Add sufficient sulfuric acid to make its concentration about 0.5 *N*, 0.5 ml. of 1 per cent silver nitrate solution, and 0.5–1.0 g. of ammonium persulfate. Boil the solution for 10 minutes, cool to room temperature, filter if turbid, add 2 ml. of 0.25 per cent diphenylcarbazide solution (for a final volume of 50–100 ml.), make up to the mark, and compare against a suitable standard solution or obtain the transmittancy of the solution with a photometer.

If the ore contains relatively much vanadium the procedure given under "Silicate rocks" (p. 197) must be followed if the diphenylcarbazide method is used. In this case the filtrate from the peroxide fusion must be boiled for one-half hour to destroy all peroxide before acidification, or better, chromium should be reoxidized with persulfate after the solution is made acid.

## C. IRON AND STEEL

The following procedure<sup>14</sup> involves precipitation of the chromium with some of the iron by sodium bicarbonate from a sulfuric acid solution of the sample, fusion of the precipitate with sodium peroxide, and determination of chromium as chromate in the filtrate from the leached melt.

### ¶ Procedure

Dissolve 1 g. (for 0.05 per cent Cr) to 5 g. or more (for 0.01 to 0.001 per cent Cr) of sample in 10 per cent sulfuric acid by volume, allowing 10 ml.

<sup>14</sup> G. E. F. Lundell, J. I. Hoffman and H. A. Bright, *Chemical Analysis of Iron and Steel*. Wiley, New York, 1931; p. 300.

of acid for each gram of sample together with an excess of 10 ml. Boil the solution until the sample has dissolved, dilute to 100 ml. with boiling water, and from a buret add an 8 per cent solution of sodium bicarbonate until a permanent precipitate appears. Then add 4 ml. of bicarbonate solution in excess, boil for one minute, allow the precipitate to settle, and filter through a rapid paper. Wash the flask and precipitate two or three times with hot water. Ignite the precipitate in a nickel crucible (chromium-free) and fuse the residue with about ten times its volume of sodium peroxide. Dissolve the cold melt in water, boil the solution for 5 minutes and filter through asbestos, or less preferably, through paper. Wash with cold 2 per cent sodium hydroxide solution containing 1 per cent sodium sulfate. Transfer the solution to a suitable color comparison tube, or make up to volume and take a suitable aliquot for color comparison in any convenient way. The comparison solution should have an alkalinity comparable to that of the sample solution.

If the chromate color is very weak, the diphenylcarbazide method should be applied. In this case the solution is acidified with sulfuric acid and oxidized with persulfate as described under "Iron ore", p. 198, vanadium being separated if necessary.

#### D. BIOLOGICAL MATERIALS

##### ¶ Procedure

Ash the sample by ignition at about 500° C. (see p. 298 for details). Take a suitable weight of the ash (not more than 1-2  $\gamma$  of chromium need be present), fuse with sodium carbonate in a platinum crucible and determine chromium with diphenylcarbazide according to the directions given under Silicate Rocks, p. 196.

**Note.**—Organic matter may also be destroyed with a mixture of nitric, sulfuric, and perchloric acids. The diluted digest is boiled with silver nitrate and persulfate to oxidize chromium, permanganate is destroyed by the addition of a little hydrochloric acid, and chromium then determined with diphenylcarbazide.

## CHAPTER XV

### COBALT

The importance of cobalt in animal nutrition has led to the development of procedures for the determination of minute amounts of the element in soils, plants, and animal tissues. Most investigators have used the nitroso-R salt method (IIA) because of its high sensitivity. The thiocyanate method (IIB) is less sensitive, but very satisfactory for some classes of material.

#### I. Separations

The nitroso-R salt method requires the separation of cobalt from iron and copper and sometimes other metals such as chromium which are undesirable in relatively large amounts. Iron can be separated sufficiently completely for the purpose by extraction as ferric chloride with ether from hydrochloric acid solution.<sup>1</sup> Copper can be precipitated with hydrogen sulfide in acid solution. Sodium peroxide oxidation in hot solution serves to precipitate cobalt and bring chromium into the filtrate as chromate.

Extraction of cobalt as dithizonate from an ammoniacal citrate solution is a good method of separation from iron, chromium, vanadium, and many other metals not forming dithizonates. Dithizone extraction in dilute mineral acid solution (p. 215) separates copper, silver, mercury, etc. from cobalt (which is left in the aqueous phase). All the dithizone separations require the presence of the reacting metals in relatively small amounts so that an inordinate volume of dithizone solution will not be necessary for extraction; this condition is fulfilled by most materials in which it is necessary to determine cobalt.

Separation of small quantities of cobalt from large amounts of nickel can be effected by extracting a thiocyanate-containing solution with amyl alcohol; nickel remains in the aqueous phase. The co-extraction of iron can be prevented by reducing it to the ferrous state (*cf.* p. 204).

Cobalt has been isolated from plant materials and soil extracts by precipitation with 8-hydroxyquinoline at pH 5.1-5.2.<sup>2</sup> Iron (III) or aluminum hydroxyquinolate serves as a collector.

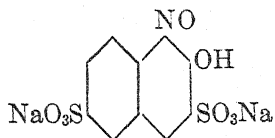
<sup>1</sup> V. North and R. C. Wells, *Ind. Eng. Chem., Anal. Ed.*, **14**, 859 (1942), separate much iron from cobalt by precipitating ferric phosphate from an acetic acid solution at pH 3.5. The iron precipitate is practically free from cobalt. These authors make use of the slight solubility of cobalt  $\alpha$ -nitroso- $\beta$ -naphtholate in dilute hydrochloric acid solution to effect further separations.

<sup>2</sup> R. O. Scott and R. L. Mitchell, *J. Soc. Chem. Ind.*, **62**, 5 (1943).

## II. Methods of Determination

### A. THE NITROSO-R SALT METHOD

Cobalt reacts with nitroso-R salt



(yellow in aqueous solution) to give a soluble red complex salt, which is stable in dilute acid solution. This reaction furnishes the most sensitive

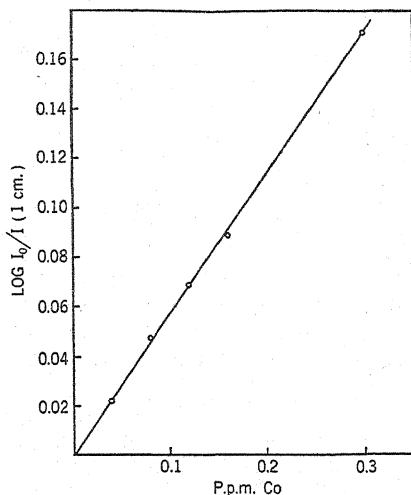


Fig. 29.—Determination of cobalt with nitroso-R salt (green filter, Cenco No. 2). (Curve based on data of Ralph A. Johnson, University of Minnesota.)

method for the determination of traces of cobalt such as occur in soils, plants, and animal organs. The cobalt complex is ordinarily formed in hot acetic acid—acetate medium. After the cobalt color has thus been developed, mineral acid (hydrochloric or nitric acid is usually used) is added to decompose the complexes of most of the other heavy metals. Iron (especially ferrous) and copper interfere if present in more than small amounts. Copper and ferric iron produce brown colors, ferrous iron a green. It has been stated that 100  $\gamma$  of copper and 1000  $\gamma$  of ferric iron<sup>3</sup> do not interfere

<sup>3</sup> By a modification of the procedure given below, it is possible to determine cobalt in the presence of much ferric iron. Thus F. W. Haywood and A. A. R. Wood, *J. Soc. Chem. Ind.*, **62**, 37 (1943), have given a procedure for determining cobalt in steel with nitroso-R salt without prior removal of iron. The sample is dissolved in a mix-

in the determination of 1  $\gamma$  of cobalt.<sup>4</sup> Small quantities of nickel, manganese, titanium, vanadium, and chromium are without effect. Cyanide, peroxide, persulfate, and reducing agents must be absent.

The procedure following is essentially that recommended by McNaught.<sup>5</sup>

#### Special Solutions

*Nitroso-R salt*, 0.1 per cent aqueous solution.

*Standard cobalt solution*, 0.0100 per cent cobalt. Dissolve 0.0404 g. of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in water, add 1 ml. hydrochloric acid, and dilute to 100 ml. From this solution prepare a more dilute one of any convenient concentration.

#### ¶ Procedure

If the sample solution contains appreciable amounts of iron, remove most of it by extracting ferric chloride from a 1:1 hydrochloric acid solution with ether. Remove copper from the suitably diluted solution by precipitation with hydrogen sulfide or by extraction with dithizone (p. 210). The solution or its aliquot should contain less than 20  $\gamma$  of cobalt.

Evaporate the solution nearly to dryness and add 1 or 2 ml. of concentrated nitric acid. Then evaporate to dryness and take up the residue in 10 ml. of water containing 0.5 ml. of 1:1 hydrochloric acid and 0.5 ml. of 1:10 nitric acid. Boil a few minutes to dissolve all solid material. Add 2.0 ml. of nitroso-R salt solution and 2.0 g. of hydrated sodium acetate. The pH of the solution should be close to 5.5 (test with bromcresol green). Boil for 45 seconds, add 1.5 ml. of concentrated hydrochloric acid, and boil further for 45 seconds. Cool the solution and determine the transmittancy at 510  $m\mu$  after dilution to a suitable volume. If the standard series method of comparison is used, as little as 0.05  $\gamma$  of cobalt can be determined when tubes 1 cm. in diameter are employed.

#### B. THE THIOCYANATE METHOD

In a medium containing a sufficient concentration of ethyl alcohol or acetone, an alkali metal thiocyanate produces a blue color with cobalt, which is due to the formation of a complex cobalt thiocyanate (possibly  $\text{Co}(\text{CNS})_4^-$  is formed). In water solution the complex is dissociated and no color is obtained unless a very large excess of thiocyanate is present.

ture of phosphoric and sulfuric acids and iron is oxidized with nitric acid, the excess of the latter being removed by evaporation of the mixture to fumes. The cobalt complex is then formed by the addition of the reagent and a suitable amount of sodium acetate. Finally other metal complexes are decomposed by addition of nitric acid and boiling.

<sup>4</sup> K. J. McNaught, *Analyst*, **64**, 23 (1939).

<sup>5</sup> K. J. McNaught, *Analyst*, **67**, 97 (1942). See also E. B. Kidson and H. O. Askew, *New Zealand J. Sci. Tech.*, **21B**, 178 (1940); H. T. Macpherson and J. Stewart, *Biochem. J.*, **32**, 763 (1938); H. R. Marston and D. W. Dewey, *Chem. Abstracts*, **35**, 3557, (1941).



Acetone is preferable to ethyl alcohol for the production of the color because a lower concentration of the former is required. According to Tomula<sup>6</sup> the color intensity reaches a practically constant maximum value in a medium containing 50 per cent by volume of acetone (final concentration of ammonium thiocyanate 5 per cent). The color intensity also depends upon the thiocyanate concentration, the increase in intensity being very rapid up to an ammonium thiocyanate concentration of 2 per cent, more gradual thereafter, but still not quite constant at 10 or 12 per cent (50 per cent acetone solution). However, the change in intensity with thiocyanate concentration at 5 or 6 per cent is so slight that one can work without difficulty at this concentration if the same amount of thiocyanate is added to unknown and standards.

The difference in cobalt concentration between the unknown and standard should not be greater than 100 per cent.

Among interfering elements may be mentioned iron (III), copper, bismuth, and nickel, as well as those metals forming slightly soluble thiocyanates or complex thiocyanates consuming the reagent. The color given by ferric iron and cupric copper can be destroyed without difficulty if not too large amounts of these metals are present by the addition of stannous chloride to a slightly acid solution. Small amounts of iron can be made harmless with phosphate.

Nickel interferes only to the extent that its green color disturbs the color comparison. If the amount of nickel is not too large, satisfactory determinations of cobalt can be obtained by using a yellow filter (see Table 24). At very low nickel concentrations the ratio of nickel to cobalt may be as large as 10 without sensible interference from the nickel. Thus 10  $\gamma$  cobalt in 5 ml. of solution can be determined accurately in the presence of 100  $\gamma$  of nickel even without the use of a filter, 1  $\times$  8 cm. tubes being used for the comparison.

When the ratio of nickel to cobalt is unfavorable, the blue cobalt compound can be extracted with amyl alcohol, the nickel being left in the aqueous solution, and the alcohol layer compared against a similar standard.

#### Special Solutions

*Ammonium thiocyanate*, 50 grams in 100 ml. of aqueous solution.

*Stannous chloride*, 20 g. of the dihydrate in 100 ml. of 2 *N* hydrochloric acid.

#### ¶ Procedure

**Acetone Method.**—Take a convenient volume of neutral or slightly acid sample and add sufficient ammonium thiocyanate solution and C. P. acetone to make their respective concentrations not less than 5 per cent and 50

<sup>6</sup> E. S. Tomula, *Z. anal. Chem.*, **83**, 6 (1931).

per cent (by volume) when the mixture is made up to volume. After mixing, compare the solution against a standard containing identical concentrations of thiocyanate and acetone and a comparable amount of cobalt ( $\pm 50\%$ ) as the unknown. If the photometric technique is applied, use a filter giving maximum transmission at 600–620  $m\mu$ .

If small amounts of ferric iron and copper are present, add enough hydrochloric acid to the sample solution to make the acidity about 2 *N* and then 3 ml. of stannous chloride for each 10 ml. of sample. Add ammonium thiocyanate and acetone as before and compare against a standard containing the same amounts of acid and stannous chloride as the unknown. When

TABLE 24  
DETERMINATION OF COBALT BY THE THIOCYANATE METHOD IN ACETONE MEDIUM  
AND BY THE AMYL ALCOHOL EXTRACTION METHOD

No. <sup>a</sup>	Procedure	Foreign metals	Co taken $\gamma$	Co found $\gamma$
1	Acetone		34	35
2	Acetone		70	70
3	Acetone		340	350
4	Acetone		3.0	2.5
5	Acetone		12.0	12.0
6	Acetone	35 $\gamma$ Ni	35	33
7	Acetone	117 $\gamma$ Ni	35	39
8	Acetone	210 $\gamma$ Ni	70	93
9	Acetone	350 $\gamma$ Ni	350	330
10	Acetone	125 $\gamma$ Ni	12.0	11.3
11	Acetone	50 $\gamma$ Cu	12.0	12.0
12	Amyl alcohol	200 $\gamma$ Ni	5	5
13	Amyl alcohol	500 $\gamma$ Ni, 100 $\gamma$ Cu	6	6

<sup>a</sup> Determinations 1–3, 6–10 by Tomula, *loc. cit.*; 4, 5, 11, 12, 13 by Sandell and Perlich, *loc. cit.* Duboscq colorimeter with greenish yellow filter used in Nos. 6–10, and 1  $\times$  8 cm. tubes in Nos. 4, 5, 11, 12, 13 (no filter).

small amounts of nickel are present (*cf.* Table 24) use a yellow or yellow-green filter.

When a Duboscq type of colorimeter is used the cobalt concentration of the final solution must be greater than 2 p.p.m. By using narrow tubes (1  $\times$  8 cm.), quantities of cobalt of the order of a few micrograms can be determined.

**Amyl Alcohol Method.**—If the sample solution contains so much nickel that a disturbing green color is produced when the acetone method is applied, it is necessary to extract the blue cobalt thiocyanate compound with amyl alcohol. Proceed as follows. Add sufficient ammonium thiocyanate to the sample solution (treated with stannous chloride as described above if small amounts of iron or copper are present) to make its concentration

30 g. per 100 ml. of solution. If amounts of cobalt in the range 1–10  $\gamma$  are to be determined the final solution should have a volume in the neighborhood of 3 ml. A 1  $\times$  8 cm. glass-stoppered tube may then be used for the extraction. Add 0.50 ml. of amyl alcohol and shake vigorously for 10–15 seconds. Allow the two phases to separate and compare the color of the amyl alcohol layer with that in similar standards, viewing the tubes transversely against a white background. In this way 5–10  $\gamma$  of cobalt can be determined with an accuracy of 10 per cent. Larger amounts of cobalt may be extracted with successive amounts of amyl alcohol, the combined extracts made up to volume and comparison made against a similar standard amyl alcohol solution.

### C. OTHER METHODS

See Table 25 for a summary of other colorimetric methods for cobalt. Some of these are sufficiently sensitive to qualify as trace methods.

## III. Special Applications

### A. SILICATE ROCKS<sup>7</sup>

The method involves decomposition of the sample with hydrofluoric-perchloric acid and extraction of the cobalt from the ammoniacal citrate solution of the residue with dithizone in carbon tetrachloride. Copper, zinc, lead, and more or less of the nickel present accompany cobalt in the dithizone separation, but ordinarily there is no interference from these metals. The carbon tetrachloride solution of the dithizonates is evaporated to dryness and the residue is ignited to destroy organic material. The oxides remaining are dissolved in acid and cobalt determined as described above in II B.

#### Special Reagents

*Sodium citrate*, 10 per cent. Usually the solution need not be shaken with dithizone (see p. 226) to remove heavy metals; the cobalt content of sodium citrate is generally insignificant.

*Dithizone*, 0.01 per cent (*w/v*) in carbon tetrachloride.

#### Procedure

Weigh 0.25 gram of finely powdered basic rock or 0.5–1.0 g. of acidic rock, into a platinum dish, add a few milliliters of water, 0.5 ml. of 70 per cent perchloric acid, and 2.5 ml. of hydrofluoric acid (for a sample greater than 0.25 g. these amounts should be correspondingly increased). Evaporate the mixture to dryness, take up the residue in 0.5 ml. of perchloric acid and 2 or 3 ml. of water, and again evaporate to dryness. To the

<sup>7</sup> E. B. Sandell and R. W. Perlich, *Ind. Eng. Chem., Anal. Ed.*, **11**, 309 (1939).

TABLE 25  
ADDITIONAL METHODS FOR COBALT

Reagent	Method	Reference
Potassium ferrieyanide + ammonia	Red color is produced. Add 10 ml. 1:1 $\text{NH}_4\text{OH}$ and 5 ml. 0.1 per cent $\text{K}_3\text{Fe}(\text{CN})_6$ to 10 ml. slightly acid or neutral test solution. Comparison can be made by colorimetric titration. Many metals interfere.	W. J. Agnew, <i>Analyst</i> , 53, 31. (1928). R. J. DeGray and E. P. Rittershausen, <i>Ind. Eng. Chem., Anal. Ed.</i> , 14, 858 (1942).
Ammonia + peroxide	Pink color (cobalt ammine). Add 2 ml. 20 per cent $\text{NH}_4\text{Cl}$ and a slight excess of $\text{NH}_4\text{OH}$ to sample, followed by 0.6 g. $\text{Na}_2\text{O}_2$ (or $\text{H}_2\text{O}_2$ ). Mix and compare against similar standard.	B. S. Evans, <i>Analyst</i> , 50, 389 (1925); W. Heinz, <i>Z. anal. Chem.</i> , 78, 432 (1929).
Dimethylglyoxime	Brown color (cobalt dimethylglyoxime) in nearly neutral solution.	S. A. Braley and F. B. Hobart, <i>J. Am. Chem. Soc.</i> , 43, 482 (1921).
Dimethylglyoxime + benzidine	Orange-red color in neutral solution.	A. Chiarottino, <i>Industria chimica</i> , 8, 32 (1933); <i>Chem. Abstracts</i> , 27, 2396 (1933).
Hydrogen peroxide + bicarbonate	Green color, possibly due to $[\text{Co}(\text{KCO}_3)_2]_2\text{O}$ . Add 0.5 ml. 3 per cent $\text{H}_2\text{O}_2$ to 10 ml. neutral solution and dilute to 50 ml. with saturated $\text{KHCO}_3$ or ammonium bicarbonate solution. As little as 4 p.p.m. of Co can be determined.	A. Blanchetière and J. M. Pirlot, <i>Compt. rend. soc. biol.</i> , 101, 858 (1929).
Sodium $\alpha$ -nitroso- $\beta$ -naphtholate	Orange-red color in ammoniacal citrate solution. Procedure described under sodium $\beta$ -nitroso- $\alpha$ -naphtholate may be used.	F. W. Atack, <i>J. Soc. Chem. Ind.</i> , 34, 641 (1915); E. G. Jones, <i>Analyst</i> , 43, 317 (1918). For determination of cobalt in the presence of much manganese by precipitation with $\alpha$ -nitroso- $\beta$ -naphthol and solution of the cobalt naphtholate in chloroform see L. Waldbauer and N. M. Ward, <i>Ind. Eng. Chem., Anal. Ed.</i> , 14, 727 (1942).
Sodium $\beta$ -nitroso- $\alpha$ -naphtholate	Add 5 ml. of ammonium citrate solution (60 g. per 100 ml.) to ca. 10 ml. of neutral cobalt solution containing up to 10 p.p.m. of Co, then 5.0 ml. of 3 M ammonia, 70 ml. of water and 3.0 ml. of 0.05 per cent reagent (0.1 g. $\beta$ -nitroso- $\alpha$ -naphthol, 1 ml. 1 M sodium hydroxide, 200 ml. water). Dilute to 100 ml. and determine transmittancy with 550 m $\mu$ filter. Copper interferes especially, nickel, chromium, and ferric iron to a lesser extent; manganese should be absent.	J. H. Yoe and C. J. Barton, <i>Ind. Eng. Chem., Anal. Ed.</i> , 12, 405 (1940).
o-Nitrosophenol	See p. 99.	
Arsenophosphotungstic acid	Indirect; reagent reduced by cobalt in basic cyanide medium (blue color).	A. Lieberman, <i>J. Am. Chem. Soc.</i> , 52, 464 (1930).
Oxalate + lead dioxide	Oxidation in acetic acid-acetate medium gives green $\text{Co}(\text{C}_2\text{O}_4)_2$ . Not sensitive.	G. H. Cartledge and P. M. Nichols, <i>Ind. Eng. Chem., Anal. Ed.</i> , 13, 20 (1941).
Terpyridyl (2,6-di-2'-pyridylpyridine)	Add 5 ml. of 0.1% terpyridyl hydrochloride solution to 25 ml. sample solution of pH 2-10; use blue-green filter. Copper, iron, and nickel interfere badly. Sensitive method.	M. L. Moss and M. G. Mellon, <i>Ind. Eng. Chem., Anal. Ed.</i> , 15, 74 (1943).

residue add 0.5 to 1 ml. of concentrated hydrochloric acid and 5 ml. of water. Heat to bring all soluble material into solution, add 5 ml. of sodium citrate solution, neutralize the cold solution with concentrated ammonium hydroxide using litmus paper, and add a few drops in excess. If there is an appreciable amount of precipitate or residue in the solution at this point, filter through a small paper, wash with small portions of water, and ignite the paper and its contents. Fuse the residue with approximately 0.1 gram of sodium carbonate, add an excess of dilute hydrochloric acid to the cooled melt, and heat to effect as complete solution as possible. Add 2 or 3 ml. of 10 per cent sodium citrate solution, make slightly ammoniacal, and reserve the solution.

To the main solution (filtrate from any insoluble material after the hydrofluoric acid decomposition), containing 5 ml. of 10 per cent sodium citrate and at least 0.2 to 0.25 ml. of concentrated ammonium hydroxide in excess (these quantities are for a 0.25-gram sample), add 5 ml. of dithizone. Shake vigorously for one-half minute and draw off the carbon tetrachloride extract. Add 2 or 3 ml. of dithizone to the solution, shake as before, and continue in this manner until the last portion of dithizone does not become red after shaking for 1 minute. In like manner extract the ammoniacal citrate solution of the sodium carbonate melt with a milliliter or two of dithizone. Wash the combined carbon tetrachloride extracts with 5 ml. of water, and run the carbon tetrachloride layer into a small silica (not porcelain) dish, being careful to avoid the transfer of any aqueous phase.

Evaporate the carbon tetrachloride, rinse the upper portion of the dish with a few drops of carbon tetrachloride to wash down any residue, and ignite at redness to destroy organic matter. Care must be taken to burn off all organic material, but too prolonged heating or too high a temperature should be avoided.<sup>8</sup> Add 2 or 3 drops each of hydrochloric and nitric acids, distribute the liquid over the interior of the dish with the aid of a stirring rod, and evaporate to dryness on the steam bath. Add to the cold dish 0.5 ml. of water and 3 or 4 drops of stannous chloride solution (20 grams of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 ml. of 2 *N* hydrochloric acid). Transfer the solution to a small glass-stoppered flat-bottomed tube (1 × 8 cm.) or a small vial. Rinse the dish with 0.5 ml. of ammonium thiocyanate (50 grams in 100 ml. of water), then with 2 ml. of reagent-quality acetone, and transfer these washings to the tube. The concentration of acetone in the final solution must be at least 50 per cent by volume. After mixing, make the color comparison against a series of standards containing the same amounts of stannous chloride, ammonium thiocyanate, and acetone as the

<sup>8</sup> If desired, organic matter can be destroyed with sulfuric-perchloric acids. See p. 228.

unknown. The percentage of cobalt in a basic rock such as a gabbro or diabase is likely to be less than 0.01 and the standards can be prepared accordingly. In acidic rocks the percentage is likely to be less than 0.001. The color of the sample solution should be pure blue, differing little if at all in hue from the standards. A greenish hue may be due to incomplete destruction of organic matter, insufficient stannous chloride to reduce copper, or the presence of much nickel.

Alternatively the cobalt determination can be made by the amyl alcohol extraction method. This method should be used when much nickel is present in the sample, and it is also recommended for acidic rocks. Transfer the cobalt solution, treated with stannous chloride as before, to a 1 × 8 cm. glass-stoppered tube, and add 1.5 ml. of ammonium thio-

TABLE 26  
DETERMINATION OF COBALT IN SILICATE ROCKS BY THE THIOCYANATE METHOD  
Acetone used in Nos. 1-6, amyl alcohol in Nos. 7-9

No.	Co present %	Co found %
1	0.0004	0.0004
2	0.0009	0.0008
3	0.0100	0.0100
4	0.0250	0.0235
5 <sup>a</sup>	0.0048	0.0045
6 <sup>b</sup>	0.0048	0.0048
7	0.0003	0.0002
8	0.00075	0.0007
9 <sup>c</sup>	0.0006	0.0006

<sup>a</sup> 0.05% Ni.

<sup>b</sup> 0.02% Cu.

<sup>c</sup> 0.05% Ni, 0.01% Cu.

cyanate solution (50 grams in 100 ml. of water) and 0.50 ml. of amyl alcohol. Treat the standards similarly. Shake vigorously for 10 to 15 seconds and compare the colors of the amyl alcohol layers by viewing the tubes transversely against a white background.

Run a blank on the reagents and apply a correction if required.

## B. SOILS

The thiocyanate method is not always sufficiently sensitive for the determination of cobalt in soils and the nitroso-R salt method is to be preferred for general use. The preliminary treatment of the sample may be carried out in different ways. Procedure (1), involving the use of dithionite, has not been tested, but is suggested on the basis of the analogous

procedure used for silicate rocks. There is every reason to believe that this procedure will give satisfactory results, but since no data are available to show its reliability, a second procedure is also given.

#### ¶ Procedure 1

Take 0.5 g. (or less for high cobalt contents) of sample and ignite gently to destroy organic material. Decompose with hydrofluoric-perchloric acid (p. 205). Take up the residue in 1 ml. of hydrochloric acid and 10 ml. of water. Extract with 0.01 per cent dithizone in carbon tetrachloride or chloroform to remove copper (*cf.* p. 215). Then add sodium citrate and excess ammonia as described on p. 207 and extract the cobalt and other reacting metals with dithizone. Evaporate the carbon tetrachloride extracts to dryness and destroy the dithizonates by sulfuric-perchloric acid oxidation as described on p. 228. Then proceed according to the general procedure (p. 202).

#### ¶ Procedure 2<sup>9</sup>

Fuse 1 g. (or more for low cobalt contents) of finely divided sample with sodium carbonate in platinum according to the usual procedure for the decomposition of silicates. Treat the cold melt with dilute nitric acid and evaporate the liquid to dryness. Take up the residue in dilute nitric acid, warm, filter off the silica, and wash the precipitate with a little dilute nitric acid.<sup>10</sup>

Concentrate the filtrate to 100–150 ml., add 4 *N* sodium hydroxide until the solution is nearly neutral, and pour slowly with stirring into a cold aqueous solution of sodium peroxide (2 g. in 100 ml.). Heat the mixture at 100° until the precipitate settles, cool for 15 minutes, filter, and wash the precipitate first with 0.2–0.3 *N* sodium hydroxide solution containing a little sodium sulfate and then with a little water. Dissolve the precipitate in hot 1:1 hydrochloric acid and dilute the solution to 100 ml. in a volumetric flask with the same acid. Take a 25 or 50 ml. aliquot (or the whole solution when the cobalt content is low) and extract several times with an equal volume of ether to remove practically all of the iron. Evaporate the extracted solution just to dryness, dissolve the residue in 0.5 ml. of 1:1 hydrochloric acid and 5–6 drops of nitric acid, dilute to 10–15 ml., boil for a few minutes, cool, and proceed as described above in the general procedure.

<sup>9</sup> A. M. M. Davidson and R. L. Mitchell, *J. Soc. Chem. Ind.*, **59**, 232 (1940).

<sup>10</sup> In the most exact work the silica should be ignited and hydrofluorized to recover any cobalt it may contain. Usually cobalt shows but little tendency to be retained by the silica.

## C. BIOLOGICAL MATERIALS

Two procedures are given below for the determination of cobalt in animal tissues, plant material, etc. The author does not have sufficient data to recommend one procedure over the other. Recoveries of 90 to 105 per cent of the added cobalt have been obtained by the first method with as little as 0.2  $\gamma$  of the element.<sup>11</sup> The second procedure is similar to one described by Sylvester and Lampitt<sup>12</sup> for foods, except that the preliminary separation of cobalt by precipitation with  $\alpha$ -nitroso- $\beta$ -naphthol carried out by these authors is not made.

## ¶ Procedure 1

To 10 g. of dry material in a silica dish add 20 ml. of water and 10 ml. of concentrated nitric acid. Boil gently until the volume is reduced to about 15 ml., then cool and add 20 ml. of concentrated sulfuric acid. The reaction is vigorous. Cool for a few minutes, add a few ml. of nitric acid, heat gently and then more strongly until brown fumes cease to come off and further charring begins. Repeat the nitric acid treatment until after evaporation to fumes the liquid is colorless. Then fume off the sulfuric acid and heat the residue for 5 minutes in a muffle at 500°. Take up the residue in 10 or 15 ml. of 1:1 hydrochloric acid and heat for a short time at 100°. Remove iron by extracting the ferric chloride with ether from the cold hydrochloric acid solution. Dilute the extracted solution with water to reduce the acidity to about 1 *N* and precipitate copper with hydrogen sulfide. Boil the filtrate from the copper sulfide precipitation to expel hydrogen sulfide, add 1 ml. of nitric acid and evaporate just to dryness. Proceed with the determination of cobalt with nitroso-R salt as described above in the general procedure (p. 202).

## ¶ Procedure 2

Take a weight of sample sufficient to contain 1 to 10  $\gamma$  of cobalt and wet-ash in a platinum or silica dish with nitric and sulfuric acids (cf. above); finally heat to 500–550° in a muffle. Dissolve the ash in 15 ml. of 1:1 hydrochloric acid, evaporate to dryness, and take up the residue in 5 ml. of 1:4 hydrochloric acid. Filter off any insoluble material, wash with water, and dilute the filtrate and washings to 20 ml.

Extract with 5 ml. portions of dithizone (0.01 per cent in carbon tetrachloride) to remove copper. When all of the copper has been extracted the green color of the dithizone will not change on shaking. Next add 10 ml. of 10 per cent sodium citrate and enough concentrated ammonia to

<sup>11</sup> K. J. McNaught, *Analyst*, **64**, 23 (1939).

<sup>12</sup> N. D. Sylvester and L. H. Lampitt, *J. Soc. Chem. Ind.*, **59**, 57 (1940).



make the solution basic (litmus) followed by  $\frac{1}{4}$  ml. in excess. Extract the solution with 5 ml. portions of dithizone until the carbon tetrachloride layer shows no reddish color. Evaporate the extracts to dryness in a small beaker or flask, add 0.5 ml. of sulfuric acid and 5 drops of perchloric acid, heat to destroy organic matter, and remove most of the acid by continuing the heating until violent fuming ceases. The residue should be colorless. Determine cobalt with nitroso-R salt according to the general procedure on p. 202, omitting, however, the preliminary evaporation with nitric acid. Dilute to 20 or 25 ml. if a photometer is to be used. Filter the solution if it is not clear and evaluate the color in any convenient way.

## CHAPTER XVI

### COLUMBIUM AND TANTALUM

These elements are lacking in sensitive characteristic color reactions, and their determination in minute amounts is rendered still more difficult by the lack of good methods for the isolation of traces. The tannin method of Schoeller<sup>1</sup> and his coworkers for the separation of these elements from each other and from other elements is intended mostly for use on samples in which columbium and tantalum make up a considerable fraction of the whole.

#### Columbium

Columbium is more amenable than tantalum to colorimetric determination. The most characteristic reaction of columbium is that with hydrogen peroxide, which in a strong sulfuric acid solution produces a yellow color.<sup>2</sup> Unfortunately this reaction is not very sensitive. The color given by titanium under these conditions is greatly weakened by the addition of concentrated phosphoric acid (enough to make its concentration 40–50 per cent by volume), whereas the color given by columbium persists. Tantalum yields no color, even in the absence of phosphoric acid. The smallest amount of columbium that can be detected visually when 0.5 ml. of sample solution (as of a potassium hydroxide fusion) is treated with 0.25 ml. of 3 per cent hydrogen peroxide and 5 ml. of concentrated sulfuric acid amounts to about 0.02 mg. (examination in a 1.8 × 15 cm. color comparison tube). The very faint yellow color remains when 5 ml. of phosphoric acid is added. Under the same conditions (phosphoric acid present), 0.5 mg. of titanium yields a very faint color equivalent to 0.02–0.04 mg. of columbium. However, even larger amounts of titanium may be present if its effect is compensated by the addition of a like amount to the comparison solution. The quantity of titanium in the sample can be determined with hydrogen peroxide in dilute acid solution in which columbium gives no color.

<sup>1</sup> R. C. Schoeller, *The Analytical Chemistry of Tantalum and Niobium*. Chapman and Hall, London, 1937. For the determination of small amounts (tenths of a per cent) of tantalum in columbium oxide see p. 131 of this book, and for the converse p. 132. An application of the tannin method to the determination of small amounts of columbium and tantalum in wolframite is described by J. A. Tschernichow and M. P. Karsajewskaja, *Z. anal. Chem.*, **98**, 97 (1934).

<sup>2</sup> G. Thanheiser, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, **22**, 255 (1940); P. Klinger and W. Koch, *Arch. Eisenhüttenw.*, **13**, 127 (1939).

Columbium, unlike tantalum, can be reduced to the trivalent state by various metals such as zinc and tin in acid solution. In this way a brown color is obtained which can be made the basis of a colorimetric method. Thus, Meimberg treats the sample solution in concentrated hydrochloric acid with zinc and compares with a series of similar standards.<sup>3</sup> Among other reagents for columbium may be mentioned pyrogallol<sup>4</sup> and quinalizarin. In concentrated sulfuric acid solution the latter reagent gives a red color with small amounts of columbium and also tantalum; quinalizarin alone has a violet color in sulfuric acid. This reaction is a little more sensitive than the hydrogen peroxide test. If 0.25 ml. of 0.01 per cent quinalizarin solution in acetone is added to 5 ml. sulfuric acid (> 90 per cent) containing 0.01 mg. of columbium, a reddish violet color is produced which is slightly different from that of a blank. The effect of other metals has not been studied. Minute amounts of boric and germanic acids give a blue color under these conditions.

### Tantalum

Pyrogallol gives an insensitive color test with tantalum in *acid* solution.<sup>5</sup> Columbium and titanium are said to be without effect. A number of qualitative reactions for tantalum have been described, involving the use of rhodamine B, "brilliant green", gentian violet, and methylene blue.<sup>6</sup> Many metals interfere.

<sup>3</sup> E. Meimberg, *Z. angew. Chem.*, **26**, 83 (1913). This method was applied in determining columbium in tantalite. The latter was dissolved in hydrofluoric and hydrochloric acids and the bulk of the tantalum separated as potassium fluotantalate. For reduction of columbium in phosphoric acid solution with zinc see Giles, *Chem. News*, **95**, 37 (1907).

<sup>4</sup> N. F. Krivoshlykov, *Trudy LKKhTI*, **1939**, No. 7, 103; *Chem. Abstracts*, **34**, 2729. The oxides are fused with sodium bisulfate, the solution of the melt treated with ammonium oxalate and an equal volume of 5 per cent pyrogallol solution saturated with sodium sulfite added. A yellow color (not sensitive) is obtained in the presence of columbium. Titanium gives a similar color. It is said that tantalum does not interfere in alkaline solution.

<sup>5</sup> Krivoshlykov, *loc. cit.* The limit of the reaction is stated to be 0.05–0.07 mg. Ta<sub>2</sub>O<sub>5</sub> per milliliter.

<sup>6</sup> M. Y. Shapiro, *J. Applied Chem. U. S. S. R.*, **11**, 1028 (1938); *Chem. Abstracts*, **33**, 1624 (1939).

## CHAPTER XVII

### COPPER

Copper is an important trace element, and a great deal of work has been done on methods for its determination in minute amounts. The methods now available are in the main very satisfactory and leave little to be desired.

#### I. Separations

Copper must frequently be separated from other constituents of the sample before it can be determined by the methods described in II. A precipitation of copper in dilute acid solution with hydrogen sulfide immediately suggests itself as a method of separation from iron, nickel, cobalt, manganese, etc., and, perhaps less successfully, from zinc. No critical study of the separation of micro quantities of copper with hydrogen sulfide has been made. Although some workers have reported incomplete recovery of copper by this method, others have used it with apparently good results.<sup>1</sup> The isolation of copper by precipitation as sulfide in weakly acid solution has been investigated by Greenleaf,<sup>2</sup> who found lead to be a better collector than cadmium and tin (Table 27). The time elapsing between precipitation and filtration of the precipitate has a considerable effect on the completeness of the copper recovery. Thus Greenleaf found that in precipitating 5  $\gamma$  quantities of copper with hydrogen sulfide in the presence of 5 mg. of lead, the amounts recovered varied as follows depending upon the treatment after precipitation: 4.57 and 4.54  $\gamma$  when the mixture was shaken 30 minutes after hydrogen sulfide treatment; 5.41 and 4.85  $\gamma$  when the mixture stood overnight; and 4.93, 4.74, 4.57, and 4.51  $\gamma$  when it was allowed to stand 3 days. The recommended procedure for isolation of copper from solutions of decomposed foods calls for precipitation of copper sulfide from a medium having a pH of 2 and containing *ca.* 4 per cent of ammonium citrate and 5 mg. of lead as nitrate (volume 40–50 ml.). The stoppered flask is shaken for 1 hour after passage of hydrogen sulfide for a few minutes, or allowed to stand overnight. The precipitate is washed with a 0.1 N hydrochloric acid solution containing 3 per cent sodium sulfate and saturated with hydrogen sulfide.

The extraction of copper by dithizone from acid solution is a good method of separation from many metals. The equilibrium constant for keto cupric

<sup>1</sup> *E.g.*, S. Ansbacher, R. E. Remington, and F. B. Culp, *Ind. Eng. Chem., Anal. Ed.*, **3**, 314 (1931); E. J. Coulson, *J. Assoc. Official Agr. Chem.*, **19**, 219 (1936).

<sup>2</sup> C. A. Greenleaf, *J. Assoc. Official Agr. Chem.*, **24**, 337 (1941).

TABLE 27

PRECIPITATION OF COPPER AS SULFIDE WITH VARIOUS COLLECTORS <sup>3</sup>

The solution, having a volume of 50 ml., was adjusted to pH 2, hydrogen sulfide was passed in, and the precipitate filtered off immediately.

Collector	Cu taken $\gamma$	Cu found $\gamma$
Paper pulp	5.0	0.4
	10.0	9.1
	50.0	43.3
Cadmium, 5 mg.	5.0	0.5
	10.0	5.7
	50.0	46
Lead, 5 mg.	5.0	4.2, 3.5
	10.0	8.3, 11.3
	15.0	13.8
	20.0	17.8
	50.0	51.7
Tin, 10 mg.	5.0	3.2
	10.0	6.5
	15.0	8.4
	20.0	16.5

dithizonate has not been exactly determined but a somewhat rough determination has yielded the value  $K = 1 \times 10^{10}$  for:

$$K = \frac{[\text{CuDz}'_{2'}]_{\text{CCl}_4}}{[\text{Cu}^{++}]_{\text{H}_2\text{O}}} \times \frac{[\text{H}^+]_{\text{H}_2\text{O}}^2}{[\text{Dz}]_{\text{CCl}_4}^2}.$$

The determination was made in approximately 1 *N* hydrochloric acid, and concentrations instead of activities were substituted into the preceding expression.

This tentative value of  $K$  may be used to calculate the approximate completeness of extraction of copper from a 1 *N* hydrochloric acid solution. Suppose 50 ml. of 1 *N* hydrochloric acid containing 10  $\gamma$  of copper are shaken with 10 ml. of 0.01 per cent dithizone in carbon tetrachloride. How much copper will be left in the aqueous phase when equilibrium is attained? The ratio of concentrations of copper in the carbon tetrachloride and aqueous phase is given by:<sup>3</sup>

$$\begin{aligned} \frac{[\text{CuDz}'_{2'}]_{\text{CCl}_4}}{[\text{Cu}^{++}]_{\text{H}_2\text{O}}} &= K \times \frac{[\text{Dz}]_{\text{CCl}_4}^2}{[\text{H}^+]_{\text{H}_2\text{O}}^2} = 10^{10} (4 \times 10^{-4} - 3.2 \times 10^{-5})^2 \\ &= 1.35 \times 10^3. \end{aligned}$$

$$\therefore [\text{Cu}^{++}]_{\text{H}_2\text{O}} = \frac{[\text{CuDz}'_{2'}]_{\text{CCl}_4}}{1350} = \frac{1.6 \times 10^{-5}}{1350} = 1.2 \times 10^{-8}.$$

<sup>3</sup> For simplicity in calculation, it is assumed that all of the copper enters the carbon tetrachloride phase. The final result shows that this approximation is justified.

This concentration corresponds to about 0.04  $\gamma$  of copper in 50 ml. of aqueous solution. Even making allowance for the uncertainty in the value of  $K$ , it may be concluded that copper may under these conditions be practically completely extracted from 1  $N$  hydrochloric acid solution, especially if a double extraction is made. In practical work the acidity is generally 0.1–0.2  $N$  instead of 1  $N$  so that the factor of safety is further increased.

The question of the extent to which certain other heavy metals such as bismuth, zinc, nickel, cobalt, lead, etc. are extracted by dithizone in acid solution cannot be answered exactly until the equilibrium constants of these dithizonates have been determined. It may be expected that sharp separations can be made from manganese, nickel, cobalt (*cf.* p. 209), lead, and perhaps from moderate amounts of zinc (see p. 450). Ferric iron does not form a dithizonate, but it slightly oxidizes dithizone. However, moderate amounts of iron do not interfere (see p. 229).

The other metals reacting with dithizone in mineral acid solution (0.1 – 1  $N$ ) are palladium, gold, silver, mercury, and bismuth, the latter incompletely when only a moderate excess of dithizone is used in the extraction as is usually the case. So far as silver, mercury, and bismuth are concerned, the use of alkali halides or halogen acids as precipitants and complex formers permits the separation of copper from these metals although the possibilities have not been fully explored. Although the point does not seem to have been tested, it seems likely that much silver can be separated from cupric copper by precipitation as the chloride. The minute amount of silver remaining in solution probably will react very incompletely in acid chloride solution with dithizone, and still less so if a little iodide is added. Mercury (II) does not react with dithizone in a bromide solution at  $pH$  1 in consequence of the formation of slightly dissociated  $HgBr_4^-$ . The separation of copper from small amounts of mercury on the basis of this behavior has been carried out by shaking the chloroform solution of the dithizonates of the two metals (20 ml.) with 5 ml. of 40 per cent potassium bromide solution and 50 ml. of 0.25  $N$  hydrochloric acid.<sup>4</sup> Copper remains in the chloroform layer, mercury goes into the aqueous phase. Any bismuth which has been coextracted with copper from acid solution may be removed from the organic solvent layer by shaking the latter with an equal volume of 2 per cent potassium iodide solution in 0.01  $N$  hydrochloric acid.<sup>5</sup> The aqueous phase is then shaken with 5 or 10 ml. of 0.001 per cent dithizone to recover any small amount of copper which may have gone into it.

<sup>4</sup> E. P. Laug and K. W. Nelson, *J. Assoc. Official Agr. Chem.*, **25**, 399 (1942).

<sup>5</sup> C. A. Greenleaf, *J. Assoc. Official Agr. Chem.*, **25**, 385 (1942).

The following results were obtained by Greenleaf (*loc. cit.*) in applying this method (*cf.* p. 219):

Cu taken	Bi taken	Cu found
$\gamma$	$\gamma$	$\gamma$
25	0	24.6
25	500	24.5
0	500	0.0

There is a lack of data on the direct extraction of copper from an acid iodide solution (containing a reducing agent to destroy any free iodine) as a means of separation from silver, mercury, and bismuth.

The destruction of cupric dithizonate and excess dithizone in the extracts, which must precede the determination of the separated copper, may be effected by evaporating the organic solvent and heating the residue with a mixture of sulfuric and perchloric acids<sup>6</sup> until an entirely colorless solution is obtained. Alternatively, the carbon tetrachloride solution may be evaporated in a silica dish and the residue ignited to copper oxide, which then is dissolved in hydrochloric acid. The latter procedure is more rapid, but it shows a tendency to give slightly low results.<sup>7</sup>

Another possible method of destroying the dithizonate and returning copper to the aqueous solution involves shaking the carbon tetrachloride solution with an acid permanganate solution and removing the excess of the latter together with manganese dioxide by treatment with a suitable reducing agent (*cf.* p. 328). This method has not been investigated for copper, but it gives good results in the case of mercury. Bromine water (0.5 ml. + 10 ml. 5% sulfuric acid) has also been used to destroy copper dithizonate and return copper to the aqueous phase.<sup>8</sup>

Electrolytic deposition of copper is sometimes of value in the isolation of traces.<sup>9</sup>

## II. Methods of Determination

There are innumerable organic compounds that give sensitive color reactions with copper, and many colorimetric methods have been described. The two most important colorimetric reagents are dithizone and sodium diethyldithiocarbamate. Dithizone is the more sensitive reagent, but mercury and silver, as well as much iron, interfere in its direct use, and special measures must be taken when these are present. The diethyldithiocarbamate method may be applied in the presence of restricted amounts of iron as well as mercury and perhaps silver. On the other hand,

<sup>6</sup> N. D. Sylvester and L. H. Lampitt, *Analyst*, **60**, 377 (1935).

<sup>7</sup> The error will usually not exceed 10 per cent but no doubt depends on the particular conditions.

<sup>8</sup> *J. Assoc. Official Agr. Chem.*, **25**, 390 (1942).

<sup>9</sup> See, for example, F. Grendel, *Pharm. Weekblad*, **67**, 913, 1050, 1345 (1930), and also p. 26.

manganese, nickel, and cobalt interfere in the carbamate method but not in the dithizone procedure. Bismuth interferes in both procedures but less so in the dithizone method than in the carbamate. The smaller amounts of copper determinable with dithizone will frequently make it the preferred reagent in trace analysis. The dithizone method has the further advantage of being carried out in acid solution, and complications due to precipitation of calcium, and other, phosphates, which may occur in the carbamate method, are avoided.

#### A. THE DITHIZONE METHOD

Copper reacts with dithizone in dilute (0.1 *N*) mineral acid solution to form the keto complex (red-violet). Palladium, gold, silver, and mercury (I and II) react under the same conditions, as already mentioned, and must be absent. Bismuth also reacts in acid solution, although less readily than copper, and leads to error if present in more than small amounts. Ferric iron oxidizes dithizone to a certain extent and may not be present in appreciable amounts; phosphate may be expected to reduce the interference of much iron. On the other hand metals such as lead, zinc, cadmium, nickel, etc., which do not react appreciably with dithizone in 0.1 *N* hydrochloric acid, are without effect unless present in high concentrations (*cf.* p. 80). The most generally applicable procedure for the determination of copper involves its isolation from an acidic aqueous solution by a preliminary extraction with a carbon tetrachloride or chloroform solution of dithizone, if need be in the presence of bromide or iodide as complex formers, as described on p. 220 *et seq.* Such preliminary isolation of copper is a prerequisite to the general use of the directions given below. Sometimes when the amount of silver, mercury, and bismuth is small, a shorter total procedure can be used, in which a preliminary extraction of copper is not made.<sup>10</sup>

The mono-color method (p. 83), cannot readily be applied in the determination of copper, because on washing the carbon tetrachloride solution of keto copper dithizonate with dilute ammonia or other alkaline solution to remove excess dithizone, slight transformation into the enol complex (brown) occurs.<sup>11</sup> The mixed-color method gives good results. It is very

<sup>10</sup> Thus G. H. Bendix and D. Grabenstetter, *Ind. Eng. Chem., Anal. Ed.*, **15**, 649 (1943), extract the slightly acidic solution (pH *ca.* 2, phosphate-citric acid buffer) with a measured volume of 0.0015 per cent dithizone in carbon tetrachloride, and then shake the extract with a 0.01 *N* hydrochloric acid solution of 2 per cent potassium iodide to decompose the dithizonates of silver, mercury, and bismuth. Copper is thus left alone in the carbon tetrachloride layer, in which it is photometrically determined.

<sup>11</sup> Various authors, however, have described monocolour methods. Where the highest accuracy is not sought such methods may be more or less satisfactory. See, for example, J. Schwaibold, B. Bleyer, and G. Nagel, *Biochem. Z.*, **297**, 324 (1938).



rapid and simple. Either a green or a red filter may be used in obtaining the transmittancy of the copper dithizonate-dithizone solution (compare

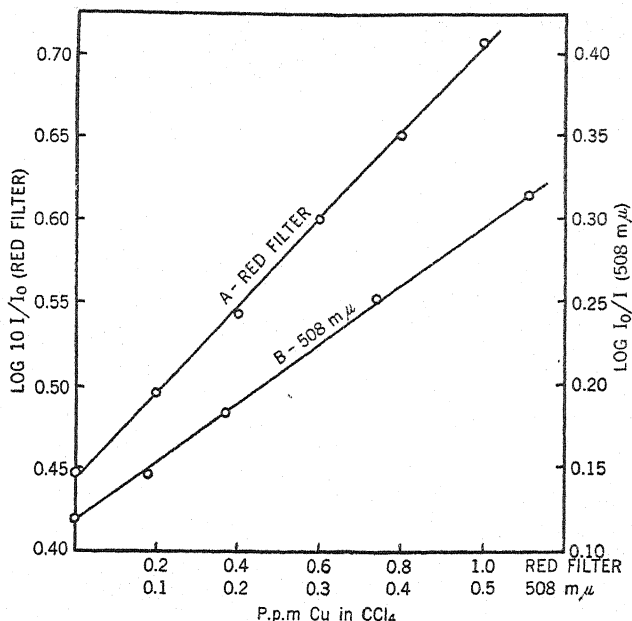


Fig. 30.—Determination of copper with dithizone. A. Transmittancy obtained with a red filter (data of S. Anonsen). B. Transmittancy determined at 508 mμ. (From data of Liebhafsky and Winslow, *J. Am. Chem. Soc.*, **59**, 1969 (1937)). Stratum thickness 1 cm. in each case.

TABLE 28

DETERMINATION OF COPPER WITH DITHIZONE BY THE MIXED COLOR METHOD  
(EFFECT OF SOME FOREIGN IONS AND HIGH ACIDITIES)

10 ml. aqueous solution (0.1 N in HCl) + 5 ml. ca. 0.001 per cent dithizone in CCl<sub>4</sub>

Addition	Cu taken γ	Cu found γ
(0.5 N HCl)	3.0	2.85
(1.0 N HCl)	3.0	2.35
10 mg. Fe <sup>III</sup>	0.0	1.5
1 mg. Zn	2.0	2.0
0.5 mg. Bi	2.0	2.5

Fig. 30 and p. 79 and 85).<sup>12</sup> Under the conditions recommended in the procedure, the relation between extinction and copper concentration is

<sup>12</sup> See H. A. Liebhafsky and E. H. Winslow, *J. Am. Chem. Soc.*, **59**, 1968 (1937), for transmission curves of dithizone-copper dithizonate mixtures in carbon tetrachloride.

practically linear up to 1 p.p.m. of copper in the organic solvent. The aqueous solution may be 0.05–0.1 *N* in hydrochloric acid but not much stronger, especially if the excess of dithizone in the mixture is only slight. It is very important that the carbon tetrachloride used be pure. A product of inferior quality may contain a substance which inhibits the reaction between copper and dithizone in acid solution, so that even after shaking for 5 minutes the reaction is incomplete.

### Reagents

*Dithizone*, 0.001–0.0012 per cent (weight/volume) in carbon tetrachloride. The latter must be reagent quality, free from any substances inhibiting the reaction with copper in acid solution. The solid dithizone need not be specially purified. As purchased, the solid generally contains 85–90 per cent dithizone.

*Water*. This must be copper-free. Since distilled water frequently contains copper, redistil in an all-Pyrex apparatus.

*Hydrochloric acid*. The analytical reagent generally is nearly copper-free, although it may contain traces of mercury. Preferably the reagent-quality acid should be redistilled, especially if minimal amounts of copper are to be determined.

*Standard copper solution*, 0.01 per cent. Dissolve 0.1964 g. of clear uneffloresced crystals of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  in water, add enough hydrochloric (or sulfuric) acid to make the final acidity about 0.1 *N* and dilute to 500 ml. From this solution prepare a weaker one (conveniently 0.002 per cent) by dilution with 0.1 *N* hydrochloric acid. Alternatively the standard copper solution may be prepared by dissolving pure metallic copper in a slight excess of 1:1 nitric acid, diluting with water, boiling to remove all oxides of nitrogen, and diluting to volume.

### Procedure

The sample solution may conveniently have a volume of about 10 ml. and should contain not more than 5  $\gamma$  of copper if 5 ml. of dithizone are to be used. Make the solution 0.05–0.1 *N* in hydrochloric (or sulfuric) acid and shake for 2 minutes in a small separatory funnel with 5.0 ml. of 0.001 per cent dithizone (delivered from a covered buret or a pipet). If the color of the carbon tetrachloride is a red-violet, an excess of dithizone may not be present; in such a case add another 5 ml. portion (or less) of dithizone and shake again. The color of the final solution should deviate from that of a pure copper dithizonate solution.

Allow a few drops of carbon tetrachloride to flow out of the funnel to displace any aqueous solution in the bore of the stopcock and dry the stem of the funnel with filter paper rolled around a thin glass rod. Deliver the carbon tetrachloride into a suitable cell and cover the latter to prevent evaporation. The solution should be entirely clear. Obtain the transmittancy either at 510  $m\mu$  (or in the range 500–550  $m\mu$ ) or 625  $m\mu$  (or in the range 600–650  $m\mu$ ). In constructing the reference curve use copper solutions having approximately the same volume and acidity as the sample

solution. The possibility of a change in the concentration of the dilute dithizone solution on standing must be borne in mind (slow decomposition, especially on exposure to light, and in warm weather, and possible evaporation of carbon tetrachloride). Once the calibration curve has been established, one or two points suffice for checking.

The standard series method may also be used in the determination of copper, in which case  $1.8 \times 15$  cm. glass stoppered flat-bottomed tubes are employed. One to 4  $\gamma$  of copper will give a suitable mixed color with 5 ml. of 0.001 per cent dithizone, although a smaller volume of dithizone will give more accurate results in the lower part of this range. By using 1 ml. of dithizone, a few tenths of a microgram of copper can be determined with considerable accuracy. If the approximate amount of copper present is not known, add only 0.5–1 ml. of dithizone, shake, and then if necessary add more until a suitable mixed color is obtained.

#### B. THE CARBAMATE METHOD

The addition of an aqueous solution of sodium diethyldithiocarbamate,  $N(C_2H_5)_2CS_2Na$ , to a slightly acid or an ammoniacal solution of a cupric salt produces a brown precipitate of the very slightly soluble copper carbamate. In very dilute solutions a colloidal suspension is obtained which is suitable for colorimetric comparison,<sup>13</sup> especially if it is stabilized by gum arabic<sup>14</sup> or similar substances. The copper carbamate is soluble in such organic solvents as amyl alcohol, amyl acetate, bromobenzene, and carbon tetrachloride. Generally one of these is used to extract the copper compound and the resulting yellow-brown solution is compared against a similar solution, or its light absorption measured. In this way any difficulties associated with the use of a colloidal suspension are avoided, the interference of certain colored substances such as iron is prevented under proper conditions, and the sensitivity can be increased.

Many of the heavy metals give slightly soluble products with diethyldithiocarbamate, most of which are soluble to a greater or less extent in the organic solvents mentioned. Some of these are white or nearly so (zinc, cadmium, mercury (II), silver, lead, tin) while others are strongly colored. Iron (III) yields a brown-black precipitate in acid or neutral medium, but does not react in ammoniacal citrate solution if the pH is 9 or above.<sup>15</sup> The chief interfering metals in the copper determination are nickel, cobalt, and bismuth,<sup>16</sup> which in ammoniacal citrate solution give greenish yellow,

<sup>13</sup> T. Callan and J. A. R. Henderson, *Analyst*, **54**, 650 (1929).

<sup>14</sup> T. P. Hoar, *Analyst*, **62**, 657 (1937).

<sup>15</sup> L. A. Haddock and N. Evers, *Analyst*, **57**, 495 (1932).

<sup>16</sup> The coloration given by bismuth is not destroyed by cyanide while that of copper is, and D. L. Drabkin, *J. Assoc. Official Agr. Chem.*, **22**, 320 (1939), has recom-

dull green, and yellow precipitates respectively and impart similar colors to the organic solvent used in the extraction. The color intensities imparted by these salts, however, are much weaker ( $1/20$ – $1/30$ )<sup>16</sup> than that given by the copper compound. The interference of nickel and cobalt can be prevented by adding 1 ml. of 0.5 per cent dimethylglyoxime solution to the sample solution before the addition of ammonia.<sup>17</sup> The nickel dimethylglyoxime precipitate is best separated by centrifugation. Cobalt remains in the aqueous layer, to which it imparts an orange color not extracted by carbon tetrachloride. Uranium yields a strong yellow-brown color with carbamate in neutral medium but not in a citrate solution containing ammonia. Manganese interferes to a considerable extent in the extraction procedure by imparting a pinkish color to the organic solvent layer. The formation of this color is associated with the air-oxidation of manganese in the basic solution, because no color is obtained if hydroxylamine hydrochloride is added. Fortunately this color is unstable, and the solution soon becomes virtually colorless if only small amounts of manganese are present; also, pyrophosphate reduces the coloration due to manganese.<sup>18</sup>

The pH of the solution has but a slight effect on the color intensity of copper carbamate in the organic solvent in the range 5.7–9.2.<sup>18</sup>

The extraction procedure given below is applicable in the presence of small amounts of iron and manganese, as well as minor quantities of zinc, lead, tin (IV), arsenic, antimony, and other metals not giving colored diethyldithiocarbamates. The interference of small amounts of iron is prevented as already mentioned by carrying out the reaction in an ammoniacal solution having a pH of 9.0–9.2. It must be pointed out that the amount of iron which may be present is limited. Some procedures described in the literature must be applied with caution because they are more subject to interference from iron than is indicated. The procedure described here allows the presence of 5 mg. of ferric iron, but not much more, in 25–30 ml. of solution containing 1 g. of ammonium citrate. Pyrophosphate probably would be more effective than citrate in preventing the interference of iron, but its use leads to difficulties in the presence of calcium which gives a precipitate in ammoniacal solution. In the presence of citrate (pH 9.0) small amounts of calcium phosphate yield no precipitate but larger amounts give a turbid solution, and results for copper then tend to be low. As much as 0.5 mg. of manganese may be present if the trans-

mended that the interference of bismuth be avoided by obtaining the transmittancies of two sample solutions, one with cyanide, the other without, thus finding copper by difference.

<sup>17</sup> L. I. Butler and H. O. Allen, *J. Assoc. Official Agr. Chem.*, **25**, 567 (1942).

<sup>18</sup> E. J. Coulson, *J. Assoc. Official Agr. Chem.*, **20**, 178 (1937).

mittancy of the carbon tetrachloride extract is determined after 20 minutes with the aid of a blue filter. It appears that appreciable amounts of zinc tend to give low results, presumably by combining with the reagent. Unfortunately the amount of diethyldithiocarbamate can not be increased without increasing the error due to iron.

Carbon tetrachloride, bromobenzene, or iso-amyl acetate may be used as extractants. Drabkin<sup>19</sup> has recommended the latter because of its low volatility and low specific gravity which enables one to dispense with separatory funnels. The writer prefers carbon tetrachloride

The relation between the copper concentration and the extinction of the organic solvent solution is linear, or very nearly so, if monochromatic light is used. With a green filter the relation was found to be practically linear

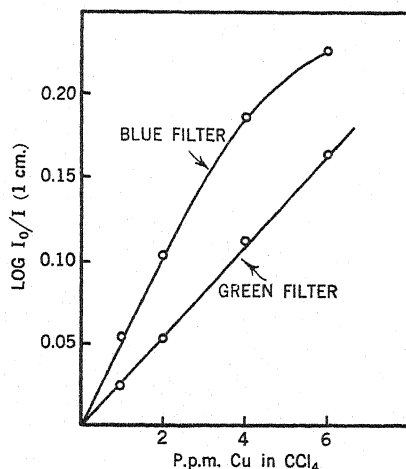


Fig. 31.—Determination of copper with sodium diethyldithiocarbamate after extraction with carbon tetrachloride (30 ml. aqueous phase, 5 ml. carbon tetrachloride).

up to a concentration of 5 p.p.m. of copper in carbon tetrachloride, and with a blue filter up to 2.5 p.p.m. The use of a blue filter permits more accurate determination of small amounts of copper than does a green filter,<sup>20</sup> and moreover the former is better when iron and manganese are present.

One portion of carbon tetrachloride does not extract all of the copper carbamate, but this of course is immaterial if the sample solution and the standard copper solutions for the construction of the calibration curve have approximately the same volume ( $\pm 5$  per cent).

<sup>19</sup> D. L. Drabkin, *J. Assoc. Official Agr. Chem.*, **22**, 320 (1939).

<sup>20</sup> The absorption maximum of copper diethyldithiocarbamate in iso-amyl acetate lies at 440  $\mu$  (Drabkin) and is about the same in carbon tetrachloride.

Solutions of copper diethyldithiocarbamate in carbon tetrachloride or iso-amyl acetate are rather stable, no appreciable change in color intensity occurring in a period of several hours; some workers have reported the solutions to be stable for 24 hours, but others have found them to fade in this time.

TABLE 29  
DETERMINATION OF COPPER WITH SODIUM DIETHYLDITHIOCARBAMATE AFTER  
EXTRACTION WITH CARBON TETRACHLORIDE

20.0  $\gamma$  Cu taken in each determination. Aqueous phase (30 ml.) contained 1 g. ammonium citrate and had pH 9.0-9.2. 1.0 ml. 0.1% sodium diethyldithiocarbamate; 5 ml.  $\text{CCl}_4$  for extraction.

Foreign substances	Cu found	
	Green filter $\gamma$	Blue filter $\gamma$
5 mg. $\text{Fe}^{\text{III}}$	19.8	20.0
10 mg. $\text{Fe}^{\text{III}}$	21.5	
0.5 mg. Mn		
Immediate reading	26	22.5
Reading after 10 min.		20.8
Reading after 20-25 min.	21.0	19.8
0.5 mg. Mn + 5 mg. $\text{Fe}^{\text{III}}$		
Immediate reading	31	23
Reading after 15 min.	23	21.0
0.5 mg. Ni	>50	
2 mg. Zn	17	16
0.5 mg. Bi	18	24
2 mg. Hg.		21.0
20 mg. Ca + 250 mg. ( $\text{NH}_4$ ) <sub>2</sub> HPO <sub>4</sub> (turbid solution)	18.5	18.0

#### Reagents

*Ammonium citrate*, 20 g. in 100 ml. of solution.

*Sodium diethyldithiocarbamate*, 0.1 per cent aqueous solution. Preserve in a brown bottle; the solution is stable for some weeks.

*Standard copper solution*. See p. 220.

#### ¶ Procedure

The sample solution may conveniently have a volume of 10-20 ml. and may contain up to 40  $\gamma$  of copper.<sup>21</sup> Not more than 5 mg. of iron or 0.5 mg. of manganese should be present. Add 5 ml. of ammonium citrate solution and adjust the pH to 9-9.2 by the addition of ammonium hydrox-

<sup>21</sup> More copper may be present if the volume of carbon tetrachloride used in the subsequent extraction is increased above 5 ml.

ide. This may be done by adding 2-3 drops of thymol blue to the solution and using a buffer solution of pH 9.0-9.2 for comparing the color. If iron is present, transfer a drop of the sample to a spot plate when the approximate desired pH has been reached, add a very small drop of indicator, and compare against a drop of buffer solution. Cool the solution to room temperature if necessary and dilute to 25 or 30 ml. ( $\pm 1$  ml.).

Add 1.0 ml. of carbamate solution and shake for 2.0 minutes in a separatory funnel with exactly 5 ml. of carbon tetrachloride. Allow the carbon tetrachloride layer to settle and when it is free from water droplets run it directly into a suitable cell, after drying the stem of the funnel with a piece of filter paper rolled around a thin glass rod. Use a blue or green filter<sup>22</sup> or preferably monochromatic light of 440 m $\mu$  wave length in obtaining the transmittancy of the carbon tetrachloride solution (see above) and keep the cell covered to prevent evaporation. If the presence of manganese in the sample solution is known or suspected, allow the carbon tetrachloride to stand for 20 minutes before determining the transmittancy.

In constructing the reference curve employ copper solutions which have been treated exactly like the sample solution, and whose final volume is the same as that of the latter.

### C. OTHER METHODS

No useful purpose would be served in listing here all the other colorimetric methods that have been proposed for the determination of copper.<sup>23</sup> Many of these methods are of slight importance from the practical standpoint. However, a few methods, of greater or less utility, may be mentioned.

The blue color given by ammonia with cupric salts is not sufficiently strong to be of much value in trace analysis.<sup>24</sup> More sensitive is the reaction with strong hydrochloric acid (yellow color) or hydrobromic acid (red-violet color),<sup>25</sup> but iron gives even a stronger color. Potassium ferrocyanide gives a moderately sensitive reaction with cupric ions; the colloidal red-brown precipitate may be stabilized with gelatin.<sup>26</sup>

Potassium ethyl xanthate gives a reaction with copper that is similar to the one produced by diethyldithiocarbamate but less satisfactory.

A method which has been much used in the past involves the extraction

<sup>22</sup> For a neutral wedge photometer a combination of Corning 511 with 038 Noviol A is recommended by Greenleaf.

<sup>23</sup> For a comparative study of many colorimetric methods for copper see R. H. Müller and A. T. Burtzell, *Mikrochemie ver. Mikrochim. Acta*, **28**, 209 (1940); *Chem. Abstracts*, **34**, 7776 (1940).

<sup>24</sup> The photometric sensitivity corresponds to about 1.5  $\gamma$  Cu per cm.<sup>2</sup> for E = 0.001 with a yellow filter.

<sup>25</sup> G. Denigès and E. Simonot, *J. pharm. chim.*, **11**, 186 (1915).

<sup>26</sup> H. Hahn, R. Juza and R. Langheim, *Z. anal. Chem.*, **110**, 270 (1937).

of copper pyridine thiocyanate,  $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_2](\text{CNS})_2$ , with chloroform or other solvent, to which a green color is imparted.<sup>27</sup>

For the use of these reagents and others such as salicylic acid, m-benzaminosemicarbazide, dithioamide, etc. see the book of Snell and Snell.<sup>28</sup> The dye Benzo Fast Yellow 5 GL (C.I. 546, diphenylurea-p,p'-disazo-bis-salicylic acid) has recently been shown to be a very sensitive reagent for copper (0.1 p.p.m. can be detected spectrophotometrically), but it is not specific.<sup>29</sup>

### III. Applications of the Dithizone and Carbamate Methods

#### A. SILICATE ROCKS

The following procedure for copper is based on one<sup>30</sup> developed for the simultaneous determination of copper, zinc, and lead in silicate rocks. The method involves separation of these and other reacting heavy metals by extraction of the basic solution of the decomposed sample with dithizone. The carbon tetrachloride solution of the dithizonates is then shaken with dilute (0.01–0.02 *N*) hydrochloric acid which decomposes lead and zinc dithizonates, transferring these metals to the aqueous phase, and leaving copper dithizonate with more or less of the nickel and cobalt in the carbon tetrachloride.

If only copper is to be determined it would be more convenient to extract it directly from the acid (0.2–0.3 *N*) solution of the decomposed sample with dithizone. There are no data available to show the reliability of this method, but it may be expected that it will be successful. The only disturbing factor is the possibility of serious oxidation of dithizone by ferric iron. It is known that ferric iron does not interfere with the separation of copper from a sulfuric acid solution (p. 229), but it remains to be seen whether the same is true for a hydrochloric acid solution such as the one that is obtained after decomposition of a silicate rock by the procedure given below.

#### Special Solutions

*Dithizone*, 0.01 and 0.001 per cent in carbon tetrachloride. See p. 220.

*Hydrochloric acid*, 6 *N*. Redistilled acid is preferable.

*Hydrochloric acid*, 0.02 *N*. Copper-free water should be used for dilution.

*Ammonia*, sp. gr. 0.9. Distil concentrated ammonia or absorb the tank gas in water. Keep in a waxed bottle.

*Sodium citrate*, 10 per cent. Dissolve 10 g. of trisodium citrate in 100 ml. of water, add 0.5 ml. of ammonia, and shake with small portions of 0.01 per cent dithizone until

<sup>27</sup> R. Biazzo, *Ann. chim. applicata*, **16**, 96 (1926).

<sup>28</sup> F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Vol. I. Van Nostrand, New York, 1936; p. 143.

<sup>29</sup> E. I. Stearns, *Ind. Eng. Chem., Anal. Ed.*, **14**, 568 (1942).

<sup>30</sup> E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **9**, 464 (1937).



the carbon tetrachloride is colored only faintly pink. Store the solution in a wax-lined bottle.

### ¶ Procedure

Weigh 0.25 g. of 100-mesh rock powder into a platinum dish and add 0.5 ml. of 70 per cent perchloric acid, 3 ml. of water, and 2–3 ml. of hydrofluoric acid. Heat on a low temperature hot plate, stirring occasionally with a platinum wire if caking occurs, until the solution has evaporated to dryness and the excess perchloric acid has been expelled. Add 0.5 ml. of perchloric acid together with a milliliter or two of water, again evaporate to dryness, and expel the excess of acid. To the residue add 2 ml. of 6 *N* hydrochloric acid and 5 ml. of water, and warm, if necessary, to bring all soluble material into solution. Next add 5 ml. of sodium citrate solution, cool to room temperature, and add ammonia dropwise until the solution is basic to litmus paper, and finally an excess of 0.25 ml. If the solution becomes turbid on the addition of ammonia, it is advisable to let it stand 10 minutes before beginning the filtration as described in the next paragraph.

TABLE 30  
DETERMINATION OF COPPER IN SILICIC AND SUB-SILICIC SILICATE ROCKS BY THE  
MIXED-COLOR DITHIZONE METHOD

Cu present or added, %.....	0.003	0.0080	0.012	0.014	0.026
Cu found, %.....	0.0025	0.0085	0.011	0.015	0.024

Filter the solution through a small paper of medium texture, transfer any residue in the dish to the paper and wash with three or four 1 ml. portions of water containing a drop of ammonia and sodium citrate solution. If the filtrate becomes turbid on standing, refilter it. Reserve the filtered solution (solution 1). Ignite the paper and its contents in a platinum crucible, avoiding an unnecessarily high temperature. Mix the residue with 0.15 g. of sodium carbonate and fuse. Add 2–3 ml. of water to the melt and warm to hasten disintegration. Filter through a small paper filter, keeping most of the residue in the crucible, and wash with 8–10 ml. of water. Reserve the filtrate (solution 2), transfer the paper to the crucible previously used, ignite, and add 0.5–1 ml. of hydrofluoric acid and 2 drops of perchloric acid to the residue. Evaporate to dryness, expel the excess of perchloric acid, add a few drops of water and one of perchloric acid to the residue, and evaporate as before. To the residue add 0.5–1 ml. of 6 *N* hydrochloric acid and a few milliliters of water and warm. (If there is a residue at this point and lead is also to be determined, filter it off and fuse it with sodium carbonate.) Add 0.5 ml. of sodium citrate and make basic with a few drops of ammonia in excess (solution 3).

Transfer the main solution (solution 1) to a separatory funnel and shake for one-half minute with 0.1 per cent dithizone solution; if the carbon tetrachloride is green at the end of this time shake for an additional half minute. Draw off the carbon tetrachloride into another separatory funnel, leaving a few drops in the first funnel to prevent loss of aqueous phase. Unless the separated carbon tetrachloride is distinctly green, add another 5 ml. portion of dithizone and shake well for  $\frac{1}{2}$ – $\frac{3}{4}$  minute. Draw off the carbon tetrachloride and continue to extract until the last portion of dithizone remains distinctly green. Next extract the solution of the leached sodium carbonate melt (solution 3), using 2 ml. portions of dithizone, and combine these extracts with the others. Finally, as a precautionary measure, extract the filtrate from the sodium carbonate leach (solution 2), after adding 0.5 ml. of sodium citrate and hydrochloric acid to give a greenish color with a drop of thymol blue.

Shake the combined carbon tetrachloride extracts for a few seconds with about 3 ml. of water to which has been added a small drop of ammonia (to remove any droplets of iron-containing solution which would otherwise interfere if lead is also to be determined), and run the carbon tetrachloride into a clean separatory funnel. Shake the extract vigorously for 1 minute with 10 ml. of 0.02 *N* hydrochloric acid. If the carbon tetrachloride remains red on shaking and does not become greenish or purple, add sufficient dithizone to impart a purplish color to the mixture and shake again for 1 minute. Draw off the carbon tetrachloride into another separatory funnel and shake for 2 minutes with a fresh 10 ml. portion of 0.02 *N* hydrochloric acid. Combine the acid extracts, add a few drops of carbon tetrachloride to rinse out any droplets of colored carbon tetrachloride, and reserve this solution for the determination of zinc (p. 457) and lead (p. 296).

Evaporate the carbon tetrachloride containing copper dithizonate to dryness in a 50 or 100 ml. Pyrex Erlenmeyer flask, add 0.75 ml. of concentrated sulfuric acid and 0.2 ml. of 70 per cent perchloric acid to the residue, and heat at 200–250° C. until the solution is entirely colorless. Cool, dilute with 10 ml. of water, neutralize with 1:1 ammonia, using methyl orange as indicator, add a drop of 6 *N* sulfuric acid in excess, and after cooling dilute to 25 ml. in a volumetric flask.

Determine copper according to the general procedure given on p. 220. For copper contents in the range 0.001 to 0.01 per cent, a 5 ml. aliquot is suitable when 5 ml. 0.001 per cent dithizone is used (photoelectric photometer); for higher percentages the size of the aliquot must be reduced or a larger volume of dithizone used.

## B. STEEL

Copper may be separated by precipitation with hydrogen sulfide in acid solution<sup>31</sup> or by extraction with dithizone. The latter procedure is a convenient one and is described below. The separated copper may be determined either with dithizone or sodium diethyldithiocarbamate as preferred; the former reagent is used in the following procedure.

## ¶ Procedure

Dissolve 0.2–0.25 g. of steel (0.01–0.1 per cent copper) in a mixture of 4 ml. 6 *N* sulfuric acid and 10 ml. of water, heating gently. When action has ceased add 0.5 ml. of concentrated nitric acid and boil for 1–2 minutes to expel oxides of nitrogen. Cool and dilute the solution to 100 ml. in a volumetric flask. Transfer 20 ml. of the solution to a small separatory funnel and shake for 1 minute with 5 ml. of 0.01–0.015 per cent dithizone

TABLE 31  
DETERMINATION OF COPPER IN STEEL WITH DITHIZONE

Bureau of Standards sample No.	Copper present %	Copper found %
9c	0.020	0.020
10d	0.010	0.010
111	0.122	0.126
33b	0.114	0.116
Synthetic sample (56% Fe, 33% Ni, 11% Co)	0.0055	0.0050

in carbon tetrachloride. The color of the extract gives an indication of the amount of copper present. Draw off the extract into another separatory funnel, and extract the solution with another 5 ml. portion of dithizone. The second extract should show practically the same color as the original dithizone; if it does not, extract a third time with another 5 ml. portion to insure the complete recovery of copper.

Shake the combined extracts for a few seconds with 5 ml. of water to which 1–2 drops of 6 *N* sulfuric acid has been added, and run the carbon tetrachloride into a 50 or 100 ml. Pyrex Erlenmeyer flask; rinse the funnel with a few milliliters of carbon tetrachloride to displace any remaining dithizone solution. Evaporate the carbon tetrachloride solution to dryness, and add 0.75 ml. of concentrated sulfuric acid and 0.25 ml. of perchloric acid to the residue. Heat at about 250° C. until the acid is entirely

<sup>31</sup> G. E. F. Lundell, J. I. Hoffman and H. A. Bright, *Chemical Analysis of Iron and Steel*. Wiley, New York, 1931; p. 267.

colorless (approximately 15 minutes heating is required). Cool, dilute with 10 ml. of water, add a drop of methyl orange, and approximately neutralize with pure ammonium hydroxide (1:1). Finally add a drop of 6 *N* sulfuric acid in excess. After cooling dilute to 25 ml. in a volumetric flask.

Depending upon the probable copper content of the sample, transfer 10 ml. (0.01 per cent copper) or 1–2 ml. (0.1 per cent copper) of solution to a small separatory funnel, add 0.20 ml. of 6 *N* sulfuric acid, and if necessary dilute to about 10 ml. with water. From a covered buret run in 5.0 ml. of 0.001–0.0012 per cent dithizone in carbon tetrachloride and shake for 2.0 minutes. If the carbon tetrachloride solution assumes the full red-violet color of cupric dithizonate run in another 5.0 ml. (or 10 ml.) of dithizone so that after shaking for 2 minutes a mixed color is obtained. Dry the stem of the funnel and deliver the carbon tetrachloride into a suitable cell. Determine the transmittancy of the solution (p. 220). Run a blank through the procedure.

### C. WATER

The carbamate method is usually directly applicable to the determination of copper in natural waters because interfering substances are not likely to be present.

#### ¶ Procedure

Acidify 50 ml. of water ( $\text{Cu} > 0.1$  p.p.m.) with hydrochloric acid (methyl orange as indicator) to insure the presence of copper in the ionic form.<sup>32</sup> Add 5 ml. of 20 per cent ammonium citrate solution and an excess of 2 ml. of concentrated ammonia. Shake with 5 ml. of carbon tetrachloride after the addition of 1 ml. of 0.1 per cent sodium diethyldithiocarbamate solution, and determine the transmittancy of the extract (see p. 225).

If the standard series method is to be applied, use  $1.8 \times 15$  cm. glass-stoppered flat-bottomed tubes with 10–15 ml. of water treated with proportionate amounts of the reagents mentioned above and shake with 1.0 to 2.0 ml. of carbon tetrachloride. The volume of the standards must be the same as that of the sample.

### D. BIOLOGICAL MATERIALS

Organic matter may be destroyed in the dry or wet way but preferably by the latter. In the former method, nitric acid, sulfuric acid, or magne-

<sup>32</sup> If it is necessary to determine copper in concentrations below 0.1 p.p.m., concentrate the sample by evaporation after acidification. For the determination of the most minute traces of the metal, concentrate in a silica dish, and separate and determine copper by the dithizone method, patterning the procedure after the directions on p. 227.

sium nitrate is frequently added after carbonization to aid in the oxidation. The temperature of ignition should not in general exceed 500° C. and a lower maximum temperature is sometimes advisable. Failure to recover all the copper after dry-ashing is probably not due to volatilization but rather to partial conversion of the copper into acid-insoluble forms by reaction with the material of the vessel in which the ignition is made or with other constituents of the ash. Conerie<sup>33</sup> found that when organic samples were ashed with sulfuric acid in old etched silica dishes, appreciable amounts of copper were lost, especially when the amount of ash was small. He recommends the addition of magnesium nitrate to the sample to furnish a bulkier ash and the transfer of the latter to a Pyrex flask before dissolving in acid.

In wet ashing, perchloric acid is frequently used in conjunction with sulfuric or nitric acid or both,<sup>34</sup> but the two latter alone will usually be satisfactory. The recovery of all the copper of the sample is more certain in the wet digestion method than in dry ashing. On the other hand the blank is likely to be larger when acids are used, although if reagents of good quality are employed very little copper should be introduced. Redistilled acids should be used if possible. The use of sulfuric acid should be avoided if the sample contains much calcium, for any calcium sulfate not finally brought into solution is likely to retain copper.

If the amount of iron, manganese, calcium phosphate, etc. in the sample is small, copper may be determined directly in the solution of the decomposed material by the carbamate method.<sup>35</sup> The safest procedure, however, is to isolate the copper by the use of dithizone. Such a procedure was worked out by Sylvester and Lampitt<sup>36</sup> for the determination of copper in milk and milk powder. This procedure, somewhat altered, is the basis of that given below. These authors use sodium diethyldithiocarbamate for the final determination of copper, but dithizone may be used as well and indeed is to be preferred for samples of very low copper content.

<sup>33</sup> A. A. D. Conerie, *Analyst*, **60**, 377 (1935).

<sup>34</sup> Regarding the use of perchloric acid in the destruction of organic matter see E. Kahane, *L'Action de l'Acide Perchlorique sur les Matières Organiques. I. Généralités* (43 pp.), *II. Applications* (124 pp.). Hermann et Cie, Paris, 1934, and the brochure of G. F. Smith, *Mixed Perchloric, Sulfuric and Phosphoric Acids and their Applications in Analysis*. G. F. Smith Chemical Co., Columbus, Ohio.

<sup>35</sup> A. Eden and H. H. Green, *Biochem. J.*, **34**, 1202 (1940).

<sup>36</sup> N. D. Sylvester and L. H. Lampitt, *Analyst*, **60**, 377 (1935). Dithizone has also been used by C. A. Elvehjem and M. D. Schultze, *J. Assoc. Official Agr. Chem.*, **19**, 227 (1936).

## ¶ Procedure

**Destruction of Organic Matter.**—The size of sample taken should preferably be such that at least 1  $\gamma$  of copper is present in it, or in an aliquot, if the final determination is made with dithizone, or at least 5  $\gamma$  is present if the determination is made with sodium diethyldithiocarbamate. Follow (a) or (b) in the decomposition, but preferably (b) unless it is known that the sample is of such nature that all of the copper can be recovered by dry ashing.

(a) *Dry oxidation:* The exact procedure in ashing will depend upon the nature of the sample.<sup>37</sup> In general, transfer the sample to a silica dish<sup>38</sup> and dry or evaporate the material on a steam bath or equivalent heat source (in the case of milk add a few drops of 6 *N* sulfuric acid). Then heat carefully over a burner or on a hot plate to char the material. At this point it is frequently advantageous to moisten the residue with nitric acid or a 20 per cent solution of magnesium nitrate; the latter is especially valuable with materials difficult to ash or those furnishing only small amounts of ash. Place the dish in a muffle furnace after evaporating on a hot plate, slowly raise the temperature to 500° C. and continue to heat until all carbonaceous material has been destroyed. If difficulty is experienced in obtaining a white ash, moisten the residue with nitric acid or magnesium nitrate solution, evaporate and heat as before. Dissolve the ash in 5 ml. (or more if necessary) of 6 *N* hydrochloric acid, heating on a steam bath, and dilute with 5–10 ml. of water. If any appreciable amount of residue remains, filter it off on a small filter paper previously washed with hydrochloric acid, wash with a little dilute hydrochloric acid and water, and ignite the paper and its contents in a platinum crucible. Treat the residue with an appropriate amount of hydrofluoric acid and a drop or two of perchloric acid, and evaporate to fumes of the latter; repeat the evaporation to fuming after adding another drop or two of perchloric acid and a little water. Take up the residue in a few milliliters of water and combine with the main solution.

(b) *Wet oxidation:*<sup>39</sup> To 5 ml. of blood, 1–5 g. of wet tissue, or 1 g. of dry food material in a Pyrex tube or small Erlenmeyer flask add 1 ml. of sulfuric acid and heat to charring. Then add 3 ml. of 60–70 per cent perchloric in acid and heat until “rings of darkened mixture begin to ascend

<sup>37</sup> For directions for ashing various organic materials consult *Methods of Analysis*, 5th ed., Association of Official Agricultural Chemists, 1940; p. 397. Also see p. 298 of this book.

<sup>38</sup> A platinum or porcelain dish (or casserole) may also be used. Either should be digested with hot 1:1 hydrochloric acid for an hour or two before use.

<sup>39</sup> A. Eden and H. H. Green, *Biochem. J.*, **34**, 1202 (1940). For decomposition with sulfuric and nitric acids follow, for example, the directions given on p. 278.

the tube". Add 2-3 ml. of concentrated nitric acid and continue to heat until the solution is colorless or very nearly so and the volume is reduced to about 1 ml. Cool, add a few milliliters of water, evaporate to fumes, and dilute with 10 ml. of water after cooling.

**Isolation of Copper.**—Approximately neutralize the solution obtained in (a) or (b) with pure ammonia, using methyl orange as indicator, and add sufficient hydrochloric or sulfuric acid to make the acidity 0.1 *N*. Transfer the solution to a small separatory funnel (the volume at this point should not exceed 50 ml.). Add 5 ml. of 0.01 per cent dithizone in analytical reagent carbon tetrachloride and shake vigorously for 2 minutes. Draw off the carbon tetrachloride into another funnel and extract the aqueous solution with another 5 ml. portion of dithizone. If this portion remains green (substantially the same hue as before shaking), all the copper has been extracted; otherwise extract with more dithizone until the color of the latter remains practically unchanged.

Shake the combined extracts with 5-10 ml. of 0.01-0.02 *N* hydrochloric acid and transfer the carbon tetrachloride to a 50 or 100 ml. Pyrex Erlenmeyer flask. Evaporate to dryness and add 0.75-1 ml. of concentrated sulfuric acid and 0.2 ml. of 70 per cent perchloric acid to the residue. Heat at about 200° C. until the solution becomes colorless, adding more perchloric acid if necessary.

**Determination of Copper.**—Dilute the concentrated acid from the digestion with 10-15 ml. of water (or dilute to volume and take a suitable aliquot). Approximately neutralize the solution with pure ammonia and determine copper either by the dithizone method (p. 220) or the carbamate method (p. 224). If the latter procedure is used, add only 1 ml. of 20 per cent ammonium citrate solution, since only traces of iron can be present.

Run a blank through the whole procedure.

## CHAPTER XVIII

### GALLIUM

#### I. Separations

Gallium hydroxide is appreciably soluble in ammonium hydroxide and an excess must be avoided in its precipitation. Aluminum hydroxide is a good collector for gallium hydroxide. By ammonia precipitation in the presence of ammonium chloride, gallium can be separated from such metals as the alkaline earths, magnesium, manganese, nickel and, less perfectly, from cobalt.

Gallium sulfide can be precipitated in very weakly acid solution (acetic acid-acetate) if an element such as zinc or arsenic is present. The use of the latter as collector has the advantage that it can later be eliminated by volatilization as arsenious chloride if necessary.

Sodium hydroxide in excess (0.5 *N*) provides a separation of gallium from indium,<sup>1</sup> which is precipitated as indium hydroxide. Some indium remains in solution and some gallium is carried down by the precipitate, but a fairly satisfactory separation can be obtained from much indium (*cf.* p. 237). Precipitation of ferric iron with sodium hydroxide is much less satisfactory, much gallium being coprecipitated with the ferric hydroxide; moreover precipitation of iron is not quite complete unless hydrated manganese dioxide is employed as collector. It would be expected that in the presence of aluminum the coprecipitation of gallium will be decreased, the aluminum being adsorbed in place of gallium on the ferric hydroxide.  $\alpha$ -Nitroso- $\beta$ -naphthol has been used for separating iron from gallium by precipitation of the former in an acetic acid solution,<sup>2</sup> and the reaction may be of value in trace analysis.

Precipitation of zinc as the mercuric thiocyanate<sup>3</sup> has been used as a separation from relatively much gallium<sup>4</sup> and may find application as well in the separation from minute amounts.

Gallium chloride is readily extracted from 1:1 hydrochloric acid by ether, even at very low concentrations (p. 28). The distribution coefficient  $\frac{[\text{GaCl}_3]_{(\text{C}_2\text{H}_5)_2\text{O}}}{[\text{GaCl}_3]_{\text{H}_2\text{O}}}$  is equal to approximately 17 in 6 *N* hydro-

<sup>1</sup> L. M. Dennis and J. A. Bridgman, *J. Am. Chem. Soc.*, **40**, 1552 (1918).

<sup>2</sup> J. Papish and L. E. Hoag, *J. Am. Chem. Soc.*, **50**, 2118 (1928).

<sup>3</sup> G. E. F. Lundell and N. K. Bee, *J. Am. Inst. Metals*, **8**, 146 (1914).

<sup>4</sup> L. M. Dennis and J. A. Bridgman, *J. Am. Chem. Soc.*, **40**, 1534 (1918).



chloric acid. The ether extraction provides a separation from aluminum and many other metals. Among the other metal chlorides (or other compounds) extracted are those of ferric iron, gold, thallium (III), germanium, molybdenum, arsenic, antimony, and tin (*cf.* Table 36, p. 249). Zinc and copper are slightly extracted. A drawback of the method in practical work is the coextraction of ferric chloride. Reduction of iron to the ferrous state may overcome this difficulty.

The extraction of gallium 8-hydroxyquinolate with chloroform provides some interesting possibilities in separations but the extraction has not been

TABLE 32  
DETERMINATION OF GALLIUM BY THE QUINALIZARIN METHOD<sup>a</sup>

Foreign element mg.	Ga taken $\gamma$	Ga found $\gamma$
Al, 10	0.0	0.0
Al, 10	5.0	4.7
Al, 10	10	11
Al, 20	10	7.5
Fe, 0.5	10	9
Fe, 1.0	20	20
Fe, 2.0	10	5
In, 100	10	11
Zn, 25	5	6
Zn, 20; Fe, 1.0	5	4
Al, 15; Fe, 1.0	10	8
Pb, 100	10	12
Cu, 100	10	10
Sn, 100	50	53
Ge, 30	10	8

<sup>a</sup> Representative values from Willard and Fogg,<sup>5</sup> chosen to show performance of method with 10  $\gamma$  quantities of gallium; larger quantities of gallium show smaller percentage error.

investigated sufficiently as yet to enable any definite statements to be made (see p. 239).

The volatility of gallium chloride (b.p. 215° C.) may occasionally be put to use in separating gallium, *e.g.*, from zinc and indium chlorides (Dennis and Bridgman, *loc. cit.*). Gallium yields a very slightly soluble precipitate with ferrocyanide in dilute hydrochloric acid; zinc can probably be used as a collector. A number of metals, including lead, copper, tin, antimony, and platinum can be precipitated by metallic cadmium, gallium being left in solution (p. 238). Precipitation of aluminum with sodium fluoride has been used to separate most of the aluminum from gallium (p. 237). Cupferron precipitates gallium in acid solution.

## II. Methods of Determination

### A. THE QUINALIZARIN METHOD<sup>5</sup>

Quinalizarin (p. 101) yields a pink to amethyst lake with gallium hydroxide. The reaction is highly sensitive (0.02 mg. of Ga per liter can be detected) but very unspecific, so that separation of most other metals is required before it can be applied. The best results are obtained when the determination is made at a pH of 5 in a solution containing ammonium acetate (1 N) and ammonium chloride (0.5 N).

The reaction of aluminum, beryllium, titanium, zirconium, thorium, rare earths, tin (IV), thallium (III), etc. with quinalizarin at pH 5.0 can be inhibited by the addition of fluoride, which in regulated excess has hardly any effect on the gallium reaction. Fluoride does not prevent the reaction of iron (III), tin (II), antimony (III), copper, lead, indium, germanium, vanadium (IV and V), and molybdenum (VI). Magnesium, manganese, iron (II), mercury (II), thallium (I), cadmium, tungsten, uranium (VI), and arsenic (V) do not give a color with quinalizarin at pH 5; other metals such as nickel, cobalt, etc. interfere only because of their own color. Zinc does not react if present in amounts less than 0.5 g. per liter. Metals such as silver, mercury (I), bismuth, columbium, etc. precipitate as chlorides or hydrolyze out, and the amounts left in solution do not interfere. Citrate, oxalate, and tartrate prevent the reaction of gallium as well as ferric iron and aluminum. Phosphate reduces the sensitivity of the gallium reaction.

The procedure following is that of Willard and Fogg. Because of the varied nature of the separations required, the procedure has been divided into sections. Aluminum is precipitated as sodium fluoaluminate and gallium then determined in the filtrate. Iron and indium are precipitated as the hydroxides with manganese dioxide as collector by an excess of sodium hydroxide. The weakness of the method lies in the difficulty of achieving a separation of iron and gallium. If more than about a milligram of iron is present, there is serious loss of gallium by coprecipitation with ferric hydroxide. The procedure becomes rather complicated if gallium must be separated from both iron and aluminum. In such a case iron is first separated with sodium hydroxide, the filtrate is acidified, aluminum and gallium hydroxides are precipitated with ammonia, the precipitate is dissolved in acid, and aluminum is separated with sodium fluoride. This particular procedure must be applied because large amounts of alkali salts interfere in the aluminum separation.

<sup>5</sup> H. H. Willard and H. C. Fogg, *J. Am. Chem. Soc.*, **59**, 40 (1937).

### Special Solutions

*Quinalizarin*, 0.01 per cent alcoholic solution. The solution should be discarded after one week. A solution 1 to 4 days old gives the best results.

*Sodium fluoride*, saturated solution in water.

*Standard gallium solution*, 0.010 mg. Ga per milliliter.

### ¶ Procedure

**In the Presence of Aluminum.**—Not more than a few milligrams of potassium or 100 mg. of sodium should be present.

Add dilute ammonium hydroxide to the solution until a turbidity appears, clear the solution with 6 *N* hydrochloric acid and add an excess of 4 ml. Next dissolve 7.7 g. of ammonium acetate and 2.7 g. of ammonium chloride in the solution and dilute to 70–80 ml. Heat to 70–80° and add with stirring sufficient sodium fluoride solution to precipitate the aluminum as  $\text{Na}_3\text{AlF}_6$  and leave an excess of 0.5 g. per liter. The precipitate should be finely crystalline. Allow the mixture to stand for an hour with occasional stirring, add a little filter paper pulp, filter off the precipitate, and wash with small portions of water containing a few drops of sodium fluoride solution. Dilute the filtrate almost to 100 ml., adjust the *pH* to 5.0 (quinhydrone electrode) and make up to 100 ml. Take an aliquot containing 1 to 10 micrograms of gallium if the color comparison is to be made in 50 ml. Nessler tubes. Prepare a series of standards containing the same amount of ammonium acetate, ammonium chloride, and sodium fluoride as the unknown solution (the *pH* of all the solutions must be the same), and add 1.0 ml. of quinalizarin solution to each tube. Compare the colors one or two minutes after mixing.

If the concentration of aluminum is less than 15 mg. per liter, gallium can be determined directly without the preliminary precipitation of sodium fluoaluminate.

**In the Presence of Iron and Indium.**—Not more than a milligram of ferric iron may be present; as much as 100 mg. of indium is permissible.

Heat the solution, having a volume of 25 ml. or less, to boiling and add enough 4 *N* sodium hydroxide to make the final concentration 0.5 to 1 *N*. Continue boiling until the precipitate coagulates, add filter paper pulp, filter, and wash the precipitate with hot 1 per cent sodium chloride solution made alkaline with sodium hydroxide (the filter paper and pulp should be washed with hot 1.5 *N* sodium hydroxide before use). Heat the filtrate nearly to the boiling point and add 0.5 ml. of 1 per cent potassium permanganate solution followed by an equal volume of alcohol to reduce the permanganate. Continue heating until the green color has dis-

appeared and a precipitate of manganese dioxide has been produced. Filter off the precipitate and wash as before.

Neutralize the filtrate to litmus with hydrochloric acid, and add enough ammonium chloride, ammonium acetate and sodium fluoride to give a solution having a pH of 5 and a salt concentration recommended in the previous section. The ammonium chloride and ammonium acetate are conveniently added as a stock solution of pH 5 containing the two salts in the respective concentrations 1.5 and 3 *N*. Then determine gallium as before.

In the case of indium it is not necessary to filter off the precipitate before adding the permanganate. If the indium concentration of the solution is less than 8 mg. per liter, a separation is not necessary (in the presence of 0.5 g. sodium fluoride per liter the limit of detection of indium with quinalizarin is 10 mg. per liter).

**In the Presence of Zinc and Aluminum or Iron.**—The procedures given above may be followed.<sup>6</sup> Zinc alone gives no color with quinalizarin if present in concentrations below 600 mg. per liter provided 0.5 g. of sodium fluoride is present per liter.

**In the Presence of Iron and Aluminum.**—Separate iron as described above, and acidify the filtrate with hydrochloric acid. Precipitate aluminum and gallium with ammonia by the usual method, avoiding any large excess of ammonium hydroxide which might redissolve some gallium. Collect the precipitate in a Gooch crucible containing a layer of purified anthracene or phenanthrene.<sup>7</sup> (Filter paper cannot be used for the filtration because it contains traces of iron extracted by hydrochloric acid.) Transfer the anthracene mat and the precipitate to the precipitation beaker and boil with dilute (6 *N*) hydrochloric acid to dissolve the hydroxides. Filter through a small filter paper, previously thoroughly washed with hot 6 *N* hydrochloric acid, to remove the filtering medium. Precipitate aluminum in the filtrate and proceed further as already described.

**In the Presence of Lead, Copper, Tin Antimony, Germanium and Platinum.**—First remove germanium by boiling the solution strongly acidified with hydrochloric acid. Reduce the acidity of the remaining solution to the point where the hydrolyzable metals will just stay in solution and add a slight excess of pure 40- to 60-mesh cadmium metal. Stir until precipitation is complete, and filter off the excess cadmium and the

<sup>6</sup> In the iron separation enough sodium hydroxide to dissolve the zinc hydroxide must be added.

<sup>7</sup> Purify by dissolving in hot acetone and pouring with stirring into an equal volume of concentrated hydrochloric acid. Wash with hot dilute hydrochloric acid and then hot water, and recrystallize the product from acetone and toluene. A hydrochloric extract of the purified material should give no color with quinalizarin under the conditions of the gallium determination.

precipitated metals. Add 2 ml. of concentrated sulfuric acid to the filtrate and evaporate to fumes to expel hydrochloric acid. Take up the residue in 75–100 ml. of water and remove cadmium from the solution by electrolysis. Precipitate traces of cadmium and other metals with hydrogen sulfide, filter, and treat the filtrate as already described.

There are no satisfactory methods for separating gallium from vanadium and molybdenum according to the authors.

#### B. THE 8-HYDROXYQUINOLINE METHOD (FLUORESCENCE)<sup>8</sup>

Gallium 8-hydroxyquinolate can be extracted from an aqueous solution having a pH as low as 2.6–3.0 by shaking with chloroform. The chloroform phase shows a strong yellowish fluorescence in ultraviolet light. Aluminum hydroxyquinolate is not extracted at this pH. Indium reacts slightly at pH 3.0, being partially extracted and imparting a fluorescence to the chloroform; at pH 2.6 (biphthalate buffer) 1 mg. of indium in 5 ml. of aqueous solution imparts a doubtful fluorescence to 1 ml. of chloroform.

The quantitative application of the gallium-hydroxyquinoline reaction has not been studied to any extent, but preliminary experiments show that gallium can be determined in this way in the presence of aluminum and iron (after reduction to the ferrous state). Copper (II), vanadium (V) and molybdenum (VI) interfere by reacting with 8-hydroxyquinoline and being extracted at pH 2.6–3.0; the reagent is thus consumed and the gallium fluorescence is weakened. However, a chloroform solution of the hydroxyquinolates of copper, vanadium, and molybdenum does not fluoresce. Much lithium gives a slight fluorescence (100 mg. of Li is equivalent in fluorescence intensity to 0.1  $\gamma$  of Ga) as does also beryllium (10 mg. of Be is equivalent to 0.1–0.2  $\gamma$  of Ga). Scandium gives a very weak fluorescence. Zinc reduces the fluorescence given by gallium. Thus 1.0  $\gamma$  of gallium in the presence of 20 mg. of zinc shows approximately as much fluorescence as 0.5  $\gamma$  of gallium in the absence of zinc. Fluoride interferes, reducing the gallium fluorescence unless aluminum is present in sufficient amount to yield fluoaluminate. Citrate also inhibits the reaction. Phosphate in small amounts (less than 2 mg. P in 5 ml.) has only a slight effect on the fluorescence intensity.

#### Special Reagents

*8-Hydroxyquinoline solution, 0.1 per cent.* Warm 0.10 g. of pure reagent with 1 ml. of 4 N acetic acid until dissolved and dilute to 100 ml. with water.

*Chloroform, analytical reagent.* It should show a mere trace of fluorescence under the conditions of the determination.

#### ¶ Procedure

In the absence of iron, adjust the pH of 5 or 10 ml. of sample solution to 3.0 in any convenient way if less than 0.05 mg. of indium is present or to

<sup>8</sup> E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **13**, 844 (1941).

2.6 if 0.05–1 mg. of indium is present. Add 0.25 ml. of 8-hydroxyquinoline solution, shake vigorously with 1.0 or 2.0 ml. of chloroform in a  $1.8 \times 15$  cm. glass-stoppered flat-bottomed tube. Treat similarly a series of standards having the same pH and volume as the unknown solution, and having so far as possible an analogous composition as regards neutral salts, etc. For comparing the fluorescence of the chloroform layers use a mercury U.V. lamp with a red-purple bulb such as Westinghouse type G-5. As little as 0.1  $\gamma$  of gallium will impart a distinct fluorescence to 1 ml. of chloroform.

In the presence of iron, dissolve 0.5 g. of hydroxylamine hydrochloride in the slightly acid solution (as much as 30–40 mg. of  $\text{Fe}^{\text{III}}$  may be present in 5 ml.). Then add sodium acetate solution until a brown color appears and allow the solution to stand for 10 minutes to insure the complete reduction of iron (the solution should become practically colorless in a few minutes). Adjust the pH to 3.0 (or to 2.6 if appreciable amounts of

TABLE 33  
DETERMINATION OF GALLIUM BY 8-HYDROXYQUINOLINE METHOD

Foreign elements	Ga present $\gamma$	Ga found $\gamma$
30 mg. Al	0.0	0.0
30 mg. Al	0.1	0.1
30 mg. Al	0.5	0.55
30 mg. Al	1.0	1.0
50 mg. Al	0.5	0.4
10 mg. Fe(III)	1.0	0.9

indium may be present), add the reagent and chloroform as before, and shake. Do not shake the solution unnecessarily long because iron may then be re-oxidized. In daylight the chloroform should show only a slight brownish color, at most, due to a trace of extracted ferric hydroxyquinolate. The standards should preferably contain roughly the same amount of iron as the unknown, but this is not necessary unless the highest accuracy is desired.

If zinc is present the standards must contain the same or nearly the same amount of zinc as the unknown.

Instead of using the standard series method, one may make the comparison by fluorimetric titration. The standard solution is added in small portions to the comparison solution (which should have the same volume, acidity, etc. as the unknown solution and contain the same amount of reagent and chloroform) with shaking until the chloroform layers show the same intensity of fluorescence.

## CHAPTER XIX

### GERMANIUM

#### I. Separations

The volatility of germanium tetrachloride (boiling point  $86^{\circ}$ ) makes possible an easy separation of germanium from most elements by distillation of a 1:1 hydrochloric acid solution. Arsenic and fluorine are likely to accompany germanium into the distillate and cause errors in the subsequent colorimetric determination. Trivalent arsenic will distil over as the chloride. Even if arsenic is originally present in the quinquevalent state, some of it will distil unless an oxidizing environment is maintained. If a stream of chlorine, or chlorine and carbon dioxide, is passed through the flask during the distillation, all the arsenic will be retained in the latter.<sup>1</sup> Alternatively, potassium permanganate may be added to the flask. Another method of preventing the distillation of arsenic consists in reducing it to the arsenide by the addition of finely divided copper to the distilling flask.<sup>2</sup> Antimony is similarly reduced.

Fluorine, which will be present in traces after a hydrofluoric acid decomposition of a silicate sample, will distil over as fluosilicic acid, and the silica thus introduced into the solution will give high results in the colorimetric determination. This error is prevented by distilling off the fluosilicic acid from a sulfuric acid solution, then adding hydrochloric acid, and distilling the germanium tetrachloride.

Germanium sulfide is highly insoluble and serves well as a separation form for small amounts of the element. The sulfide is precipitated from a 6 N hydrochloric or sulfuric acid solution, which is saturated with hydrogen sulfide and allowed to stand for a day before filtration.

Germanium may be separated from much arsenic (V) by electrolytic reduction to monogermane,  $\text{GeH}_4$ , in alkaline solution.<sup>3</sup> The monogermane is carried away in a stream of hydrogen, which is led through a hot tube to give a deposit of germanium.

Germanium appears to be quantitatively coprecipitated with ferric, aluminum, etc., hydroxides.

<sup>1</sup> L. M. Dennis and E. B. Johnson, *J. Am. Chem. Soc.*, **45**, 1380 (1923); W. Geilmann and K. Brunger, *Z. anorg. allgem. Chem.*, **196**, 312 (1931); H. Lundin, *Trans. Electrochem. Soc.*, **63**, 149 (1933).

<sup>2</sup> W. C. Aitkenhead and A. R. Middleton, *Ind. Eng. Chem., Anal. Ed.*, **10**, 633 (1938).

<sup>3</sup> S. A. Coase, *Analyst*, **59**, 462 (1934).

## II. Methods of Determination

Method B below is the more sensitive of the two methods described. Arsenic may be present in relatively large amounts in Method A but must be absent in the final solution in Method B. Silicate and phosphate must be absent in both methods.

### A. THE GERMANOMOLYBDATE METHOD<sup>4</sup>

In acid solution germanate yields a soluble yellow heteropoly acid with sexivalent molybdenum, which in the solid form is stated to have the formula  $H_8 [Ge(Mo_2O_7)_6] \cdot 28H_2O$ . The sensitivity of the reaction is sufficiently high to permit the determination of 1 part of germanium dioxide in a million parts of solution. With a sufficient excess of molybdate, Beer's law holds up to a concentration of 40 parts per million of germanium dioxide.

In solutions acidified with nitric, sulfuric or acetic acid, germanomolybdate shows a maximum color intensity which is constant over a certain range of acidity, namely 0.15–0.3 *N* for nitric acid, 0.15–0.25 *N* for sulfuric acid, and 1.4–3 *N* for acetic acid. In hydrochloric acid solution a sharp maximum in color intensity is shown at about 0.1 *N*, and this acid is therefore undesirable for acidification of the solution.

The color intensity of the complex is practically independent of the ammonium molybdate concentration, provided the latter is greater than 0.1 g.  $(NH_4)_2MoO_4$  per 100 ml. Preferably a large excess of ammonium molybdate (up to 2 g. per 100 ml.) is used to increase the stability of the color.

Organic acids such as oxalic, tartaric, and citric weaken or destroy the yellow color. Fluoride weakens the color but can be prevented from interfering by the addition of aluminum or zirconium salts which form very stable complexes with fluoride. Selenious acid, selenic acid, tellurous acid, and telluric acid decrease the color intensity somewhat. Selenium can be removed by the addition of hydroxylamine hydrochloride. Boric acid, arsenious acid, antimony (III), rhenium, and the salts of the alkali metals do not interfere. Sulfide, sulfite, stannous chloride, etc. reduce the heteropoly acid, giving a blue solution. Silicic, phosphoric and arsenic acids may yield yellow solutions. Arsenic (V) does not give a color with molybdate in the cold, and does not interfere if the temperature is kept below 25° C. Since arsenate forms a more stable complex with molybdate than does germanate, an excess of molybdate must be used. As much as 0.1 g. of arsenic (V) may be present in 100 ml. of solution without ill effect; above this concentration a precipitate separates. Prac-

<sup>4</sup> I. P. Alimarin and B. N. Iwanoff-Emin, *Mikrochemie*, **21**, 1 (1936–37).



tically all of the interfering elements are separated when germanium is distilled as the chloride.

The maximum color intensity is attained within a few minutes after the addition of molybdate. The color remains constant for 15-20 minutes and then slowly decreases in intensity.

The directions of Alimarin and Iwanoff-Emin<sup>4</sup> follow.

### ¶ Procedure

In most cases germanium must first be separated by distillation as the tetrachloride, with the use of chlorine if necessary. Treat the distillate as follows. Add sodium bisulfite until the yellow color of chlorine disappears, and then bromine water until the solution becomes pale yellow; finally decolorize the solution with bisulfite. Determine the amount of free acid in 1 ml. of the solution and then adjust the acidity of the distillate to 6 *N*. Pass hydrogen sulfide into the cold solution for one-half hour and allow the mixture to stand in a stoppered flask for 24 hours. Filter off the germanium sulfide on paper, using a paraffined funnel, and wash with 6 *N* hydrochloric acid saturated with hydrogen sulfide. Dissolve the precipitate in 10 ml. of 1 per cent sodium hydroxide free from silicate and phosphate (prepare from sodium metal). Treat the solution in a silver dish with hydrogen peroxide to destroy the thiogermanate and then heat to destroy excess hydrogen peroxide. Transfer the solution to a volumetric flask of suitable volume. A solution containing 0.5 to 5 mg. of  $\text{GeO}_2$  in 100 ml. is preferable for visual comparison.

Add from 2 to 4 ml. of freshly prepared 5 per cent ammonium molybdate for 100 ml. of solution, and then enough nitric acid to give an acidity of 0.15 to 0.35 *N*. The temperature of the solution should be kept below 25° C. Prepare a standard germanium solution (from  $\text{GeO}_2$ ) at the same time in a similar manner, and compare the solutions after a few minutes.

### B. THE MOLYBDENUM BLUE METHOD

The germanomolybdate complex, like the molybdate complexes of phosphate, arsenate and silicate, may be reduced by suitable reagents to a soluble blue substance containing molybdenum in a lower valence state. Poluektov<sup>5</sup> has given a procedure based on this fact which he applied to the determination of germanium after separation as the chloride and sulfide. Ferrous sulfate is used as the reducing agent. This procedure has been modified and applied directly to the hydrochloric acid distillate of germanium.<sup>6</sup> The following procedure pertains to the determination of germanium in silicates or silicate rocks, but the general procedure may be

<sup>5</sup> N. S. Poluektov, *Z. anal. Chem.*, **105**, 23 (1936).

<sup>6</sup> A.-G. Hybbinette and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **14**, 715 (1942).

applied to samples of different nature with suitable change in details.<sup>7</sup> Beer's law is obeyed by the molybdenum blue solution up to a concentration of about 1.5 p.p.m. of germanium, but at higher concentrations the color intensity is less than demanded by the concentration.

### Apparatus

The all-glass (Pyrex) distilling apparatus of Scherrer (p. 140) may conveniently be used for the distillation of the germanium tetrachloride. The flask should preferably have a volume of 100 ml. The end of the condenser tube should be drawn to a narrow point. A test tube, drawn to a narrow taper at the lower end, is used as a receiver to hold the sodium hydroxide solution in which the germanium tetrachloride is absorbed; it should have a capacity of at least 12 ml. and should be well paraffined to prevent attack by the sodium hydroxide solution.

### Special Solutions

*Ammonium molybdate.* Dissolve 6.00 g. of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in about 35 ml. of water, add a cooled mixture of 16.0 ml. of concentrated sulfuric acid (sp. gr. 1.84) with 35 ml. of water, dilute the solution to 100 ml. with water, and preserve in a paraffined bottle.

*Ferrous ammonium sulfate.* Dissolve 10.0 g. of the hydrated salt in water containing 1.5 ml. of 6 *N* sulfuric acid and dilute to 500 ml.

*Sodium acetate.* Dissolve 67.5 g. of sodium acetate trihydrate in water and dilute to 200 ml. Keep the solution in a paraffin-lined bottle.

*Ammonium molybdate-ferrous ammonium sulfate reagent.* This solution is unstable and must be prepared immediately before use. Add successively with shaking 10 ml. of ammonium molybdate solution, 10 ml. of ferrous ammonium sulfate solution, and 25 ml. of sodium acetate solution to 50 ml. of water and dilute to 100 ml. with water. Allow the reagent to stand 5 minutes before use.

*Sodium hydroxide.* Dissolve 25 g. of analytical quality reagent as low as possible in silica in 100 ml. of water and store the solution in a paraffined bottle.

*Standard germanium solution, 0.01 per cent Ge or  $\text{GeO}_2$ .* Dissolve a weighed amount of pure dry germanium dioxide in a few milliliters of water to which a drop or two of dilute sodium hydroxide has been added, neutralize with dilute sulfuric or hydrochloric acid, add a drop or two of acid in excess, and make up to volume.

### ¶ Procedure

Weigh 1.0 g. of rock powder into a platinum dish and add a few milliliters of water, 6 ml. of 1:1 sulfuric acid, 0.5 to 1 ml. of concentrated nitric acid, and 10 ml. of hydrofluoric acid. Evaporate slowly on a hot plate until the sulfuric acid just starts to fume, cool, add a few milliliters of water and again evaporate to fumes. Repeat the addition of water and evaporation at least two times, never letting the mixture fume strongly. Transfer the decomposed sample to the distilling flask with 1:1 sulfuric

<sup>7</sup> Since silicate rocks are very low in arsenic, no special measures are included in the procedure for retaining it in the distilling flask. When appreciable quantities of arsenic are present, the distillation should be made in the presence of chlorine or alternatively of copper, as mentioned on p. 241.

acid (chloride-free) and water. The total volume of the solution should be approximately 50 ml., of which 35 ml. should be 1:1 sulfuric acid.

**Removal of Residual Hydrofluoric Acid.**—To remove traces of fluoride, bubble air slowly through the solution and raise the temperature to 140° C. Maintain the temperature at this figure during the distillation by the slow addition of water through the funnel. In this manner distil over and discard 150 ml. of liquid. Allow the distilling flask to cool, add 15 ml. of water and, while passing air through the solution, distil until a temperature of 120° is reached. Catch the distillate in a paraffined drawn-out test tube containing 1 ml. of 25 per cent sodium hydroxide solution and 1 ml. of water. Neutralize the distillate with 1:1 hydrochloric acid, using phenolphthalein as indicator, add a drop of sodium hydroxide, and then

TABLE 34  
DETERMINATION OF GERMANIUM IN SILICATE ROCKS

Sample	Germanium present <sup>a</sup> %	Germanium found %	Error %
Granite	0.0005	0.0005	0.0000
Granite	0.0010	0.0009	-0.0001
Granite	0.0030	0.0029	-0.0001
Granite	0.0058	0.0050	-0.0008
Granite <sup>b</sup>	0.00026	0.00028	+0.00002
Granite <sup>c</sup>	0.00026	0.00030	+0.00004
Diabase	0.0008	0.0007	-0.0001
Diabase	0.0014	0.0013	-0.0001
Diabase	0.0056	0.0052	-0.0004

<sup>a</sup> Includes the germanium originally present in the samples as determined by method described (0.00026% in granite, 0.00014% in diabase).

<sup>b</sup> Contained 0.05% Cl.

<sup>c</sup> Contained 0.01% As.

acidify with acetic acid and add the mixed ammonium molybdate-ferrous ammonium sulfate reagent as described below under "Colorimetric determination", except use the whole solution instead of an aliquot. Prepare the comparison solution by adding the reagent to a solution having the same composition as the neutralized distillate. If the distillate shows no color when compared against the reference solution, all hydrofluoric acid has been expelled from the solution in the distilling flask and germanium may be distilled over as described in the next section; if a color is shown distil again at 140° as already described until a negative result is obtained.

**Distillation of Germanium Tetrachloride.**—Add 2 ml. of 1:1 hydrochloric acid and 2 ml. of water to the cool contents of the distilling flask, and distil while bubbling air through the solution until the temperature

reaches  $120^{\circ}$ .<sup>8</sup> Collect the distillate in the drawn-out test tube containing 2.00 ml. of 25 per cent sodium hydroxide solution. At the end of the distillation, neutralize the solution with 1:1 hydrochloric acid, transfer to a 25 ml. volumetric flask, and make up to volume with water.<sup>9</sup>

Allow the distilling flask to cool, add 2 ml. of 1:1 hydrochloric acid and 2 ml. of water, and distil as before. Neutralize the solution, transfer to a 25 ml. volumetric flask and make up to the mark with water. With small amounts of germanium practically all is found in the first distillate but with quantities in the neighborhood of 25  $\gamma$  a small amount is found in the second distillate.

**Colorimetric Determination of Germanium.**—Prepare two standard germanium solutions as follows. Measure out two portions of germanium oxide solution containing, for example, 5 and 10  $\gamma$  of germanium, add 10 ml. of water, 1.5 ml. of 1:1 hydrochloric acid and 2.00 ml. of 25 per cent sodium hydroxide solution. Neutralize the solutions carefully with 1:1 hydrochloric acid (phenolphthalein as indicator) and dilute to 25 ml. In a similar manner prepare a blank solution for the color comparison by neutralizing 2.00 ml. of sodium hydroxide and diluting to 25 ml.

Take a 10 ml. aliquot of each standard, of the two germanium distillates and of the blank. Make each solution basic with a drop of 25 per cent sodium hydroxide and then acidify with 0.10 ml. of 1:1 acetic acid. Add 10.0 ml. of ammonium molybdate-ferrous ammonium sulfate reagent, mix and dilute to 25 ml. with water. After 15 minutes compare the germanium distillates and the standards against the blank solution in a photoelectric photometer, using a red filter. The standard series method of comparison may also be used. The color intensity of the solutions increases slowly on standing and the readings should therefore be made after the period of standing specified. Although germanium in appreciable amounts is unlikely to occur in the reagents, it is nevertheless advisable to run a blank through the procedure, especially since any contamination by silica will then be revealed.

<sup>8</sup> Approximately 5 ml. of liquid should distil over.

<sup>9</sup> With minimal amounts of germanium omit the dilution to volume and use the whole of the distillate instead of an aliquot in the subsequent colorimetric determination.

## CHAPTER XX

### GOLD

#### I. Separations

The easy reducibility of gold to the metal provides a basis for its isolation from most elements.<sup>1</sup> Gold may be readily precipitated from extremely dilute, acid solutions by such reducing agents as stannous chloride, zinc, and magnesium if a suitable collector is used.<sup>2</sup> Mercury, mercurous chloride, lead, and tellurium have been used as collectors. Tellurium is very useful for the purpose. The precipitate of elemental tellurium, produced by reduction with stannous chloride, contains the gold as telluride. The precipitate may be dissolved in aqua regia; the tellurium in the solution does not interfere if gold is determined by the rhodanine method. If tellurium must be removed, as when determination of gold with stannous chloride is to follow, the precipitate can be ignited strongly to volatilize tellurium oxide. Directions for the tellurium coprecipitation are given later in this chapter in connection with the rhodanine method for the determination of gold.<sup>3</sup> By the use of this method, gold can be separated from much iron, copper, lead, and other metals (Table 37). Palladium, platinum, mercury, and more or less silver will be coprecipitated together with the gold. Small amounts of other metals will contaminate the precipitate, but ordinarily will do no harm because only a very small quantity of tellurium need be used, and the absolute amounts of the contaminants will therefore be negligibly small.

Gold can be precipitated with various organic reducing agents such as metol, *p*-phenylenediamine, and hydroquinone<sup>4</sup> in hot 1:10 hydrochloric acid solution. Palladium, platinum, tellurium, and selenium are not

<sup>1</sup> Passing reference may be made to the familiar method of isolation used in fire assaying in which the sample is fused with a mixture of lead oxide, a reducing agent, and a "flux", whereby the gold is collected in a lead button, from which after cupellation and parting it is recovered as the pure metal. Although in this process the gold is finally weighed, there is no reason why the metal could not be dissolved and determined colorimetrically, if its amount was so small as to preclude accurate weighing.

<sup>2</sup> For an example of such a procedure see p. 253.

<sup>3</sup> W. B. Pollard, *Analyst*, **62**, 597 (1937), also uses tellurium as a collector for gold in a volumetric method, but precipitates it with sulfur dioxide from a 1:10 hydrochloric acid solution. He was able to recover 0.01 mg. of gold quantitatively from about 10 liters of solution, using 200 mg. of tellurium.

<sup>4</sup> F. E. Beamish, J. J. Russell, and J. Seath, *Ind. Eng. Chem., Anal. Ed.*, **9**, 174 (1937); J. Seath and F. E. Beamish, *ibid.*, **9**, 373 (1937).

precipitated under these conditions, and palladium and platinum at least show little tendency to contaminate the precipitate of gold. The possibility of precipitating gold in this manner from highly dilute solutions has not been investigated.

In the determination of gold in sea water, ammonium sulfide has been used as precipitant for the gold with lead sulfide as the collector.<sup>5</sup> This method permits the quantitative recovery of gold from solutions containing 1  $\gamma$  in 1000 liters. Charcoal has been used as an adsorbent for gold in its determination in the water of streams.<sup>6</sup> The charcoal is ashed after adsorption, the ash brought into solution, and gold determined with stannous chloride or rhodanine reagent (p. 252).

The extractability of chlorauric acid from hydrochloric acid medium by ethyl ether and ethyl acetate<sup>7</sup> provides not only a method of isolating small amounts of gold but also a method for separating it from palladium and platinum as well as other elements. The extraction with ether has been studied especially by Mylius<sup>8</sup> and we give some of his results in Tables 35 and 36. It should be noted that the extraction of gold becomes more difficult as its concentration in the aqueous phase decreases.

## II. Methods of Determination

Gold may be determined colorimetrically by reduction to the metal, which under suitable conditions gives fairly stable colloidal suspensions; by the formation of a slightly soluble red-colored compound with dimethyl- or diethylaminobenzylidenerhodanine, which also yields a colloidal dispersion; and by oxidation of certain organic compounds which yield strongly colored products with auric gold. All of these methods are subject to various interferences, and gold must usually be separated from the other constituents of the sample before it can be determined. The colloidal gold method has the advantage of greater specificity but is less sensitive than the other methods.<sup>9</sup> The rhodanine method may be recommended for samples free from palladium and preponderant amounts of silver.

### A. THE STANNOUS CHLORIDE METHOD

Various reagents have been used for the reduction of auric solutions to obtain a colloidal dispersion of gold suitable for use in colorimetric analysis.

<sup>5</sup> F. Haber, *Z. angew. Chem.*, **40**, 303 (1927); F. Haber and J. Jaenicke, *Z. anorg. allgem. Chem.*, **147**, 156 (1925).

<sup>6</sup> C. K. Kropachev, *Sovet. Zolotoprom.*, **1935**, No. 8, 46.

<sup>7</sup> V. Lenher and C. H. Kao, *J. Phys. Chem.*, **30**, 126 (1926).

<sup>8</sup> F. Mylius, *Z. anorg. Chem.*, **70**, 203 (1911); F. Mylius and C. Hüttner, *Ber.*, **44**, 1815 (1911).

<sup>9</sup> Except perhaps when a modification of the reduction method is employed in which the gold is reduced on the surface of solid mercurous chloride.

TABLE 35

## COMPLETENESS OF EXTRACTION OF CHLORAUIC ACID WITH ETHER

A solution containing one gram of gold as chlorauric acid in 100 ml. of water or hydrochloric acid was shaken with an equal volume of ethyl ether saturated with water.

Sample	Au in ether layer	
	H <sub>2</sub> O solution g.	10% HCl solution g.
First extraction.....	0.4031	0.982
Second extraction.....	0.197	0.017
Third extraction.....	0.108	0.0005
Fourth extraction.....	0.067	

TABLE 36

## EXTRACTION OF VARIOUS METALS AS CHLORIDES WITH ETHER

An hydrochloric acid solution containing 1 g. of the metal as chloride in 100 ml. was shaken with an equal volume of ethyl ether saturated with water.

Metal	Percentage of metal in ether layer				
	1% HCl	5% HCl	10% HCl	15% HCl	20% HCl
Au (III)	84	98	98		95
Fe (III)	Trace	0.1	8	92	99
Sb (III)	0.3	8	22	13	6
Sb (V)	Trace	25	6	22	81
As (III)	0.2	0.7	7	37	68
Te (IV)	Trace	0.2	3	12	34
Sn (IV)	0.8	10	23	28	17
Hg (II)	13		0.4		0.2
Cu (II)	Trace		0.05		0.05
Zn	Trace		0.03		0.2
Ni	Trace		Trace		Trace
Pt (IV)	Trace		Trace		Trace
Ir (IV)	Trace		0.02		5
Pd (II)	Trace		0.02		

Data obtained by other workers (see W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*. Wiley, New York, 1929; p. 107) show that the following elements are also extracted from hydrochloric acid solution: As (V), very slightly; Ga, 97%; Ge, ca. 50%; Mo (VI), 80-90%; Tl (III), 90-95%; Sn (II), 15-30%. The following metals are not extracted appreciably: Al, Be, Bi, Ca, Cd, Cr, Co, Fe (II), Pb, Mn, Ni, Os, rare earths, Ag, Ti, Th, W, U, Zr. Vanadium (IV and V) appears to be extracted in traces.

Stannous chloride is as good as, if not better than, any that have been proposed for the purpose.<sup>10</sup>

As well known, the color and stability of colloidal gold suspensions are greatly dependent upon the electrolyte concentration of the solution. The standard solutions for the construction of the reference curve or for comparison must have the same acid and salt concentration as the sample solution. Frequently this condition can be fulfilled only by isolating the gold and bringing it into solution again. Fink and Putnam<sup>11</sup> have shown the important role played by the hydrochloric acid concentration in the stannous chloride method for gold. At low acidities, 0.1 *N* or less, the colloidal solution has a yellow color and at higher acidities, in the neighborhood of 0.5 *N*, it has a purplish color, which passes into blue at still higher acidities. Color development is more rapid at low acidities than at

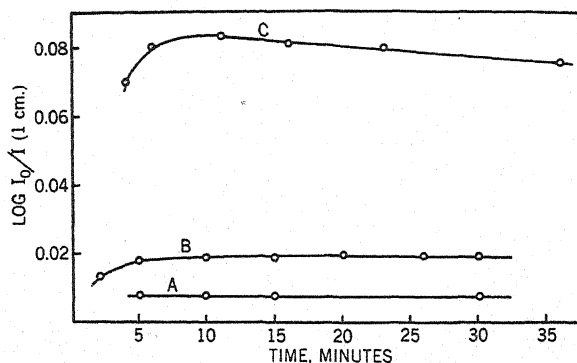


Fig. 32.—Relation between time and optical density of gold suspension in the stannous chloride method at various gold concentrations: (A) 0.44 p.p.m. (B) 1.1 p.p.m. (C) 4.4 p.p.m. Au. HCl concentration *ca.* 1 *N*.

high. Moreover the suspension formed in weakly acid solutions is more stable than that produced in more strongly acid medium. For these reasons it is advisable to work at low acidities. However, satisfactory results can be obtained at relatively high acidities. Figures 32 and 33 show the relation between color intensity on the one hand and time and concentration on the other in approximately 1 *N* hydrochloric acid solution.

Determination of gold with stannous chloride demands the absence of platinum, palladium, ruthenium, tellurium, selenium, silver (except in

<sup>10</sup> For the use of  $\alpha$ -naphthylamine hydrochloride as a colorimetric gold reagent see I. A. Paul'sen and S. M. Pevzner, *J. Applied Chem. U.S.S.R.*, **11**, 697 (1938); *Chem. Abstracts*, **32**, 6972 (1938).

<sup>11</sup> C. G. Fink and G. L. Putnam, *Ind. Eng. Chem., Anal. Ed.*, **14**, 468 (1942).



very low concentrations), mercury, and some other metals such as tungsten which give fairly strongly colored reduction products under the conditions.

### Special Solutions

*Stannous chloride*, 10 per cent solution of the dihydrate in 1 *N* hydrochloric acid. This solution should be prepared fresh weekly.

*Standard gold solution*, 0.001 per cent Au as chlorauric acid in 0.1 *N* hydrochloric acid. This solution is best prepared fresh at reasonable intervals by diluting a 0.01 or 0.1 per cent gold solution. The latter may be obtained by dissolving pure gold in a few milliliters of aqua regia, evaporating just to dryness on the steam bath, adding a milliliter or two of concentrated hydrochloric acid, evaporating nearly to dryness, and making up to volume with 1 *N* hydrochloric acid.

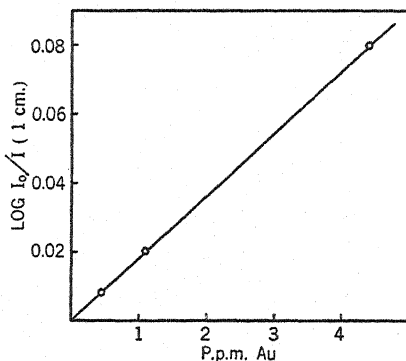


Fig. 33.—Determination of gold by the stannous chloride method. Two ml. 10 per cent stannous chloride added to 20 ml. of gold solution in 1 *N* hydrochloric acid, solution diluted to 25 ml. with water and extinction determined after 20 minutes. No filter used.

### Procedure

The sample solution may contain 10 to 100  $\gamma$  of gold (III) in a volume of 20 ml. or less, and should preferably be only slightly acid (0.05 *N* in hydrochloric acid). If necessary, however, one may work with a solution 1 *N* in hydrochloric acid. Dilute with water to about 20 ml. in a 25 ml. volumetric flask and add all at once 2 ml. of stannous chloride solution. Make up the volume to the mark with water, mix, and allow to stand 20 minutes. Then determine the transmittancy. It is hardly necessary to use a filter, although slightly lower transmittancies will be obtained with green light. The standard solutions for the reference curve must have the same acidity as the sample solution and must contain the same concentration of extraneous salts.

## B. THE RHODANINE METHOD

In slightly acid solution, *p*-diethylaminobenzylidenerhodanine (p. 103) yields slightly soluble red or red-violet products with auric gold, silver, palladium (II), platinum, mercury, and copper (I). A fairly sensitive

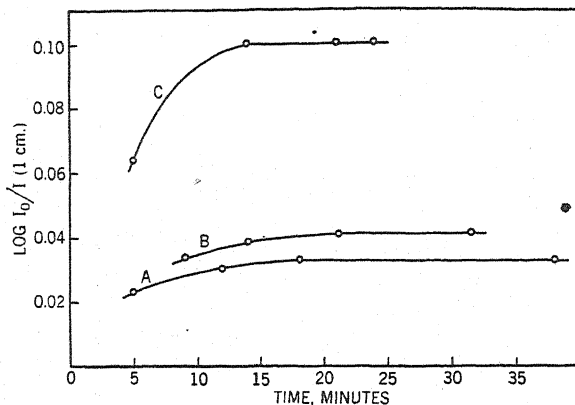


Fig. 34.—Relation between time and optical density of gold-rhodanine suspension in the *p*-diethylaminobenzylidenerhodanine method at different gold concentrations: (A) 0.44 p.p.m. (B) 0.53 p.p.m. (C) 1.32 p.p.m. Au.

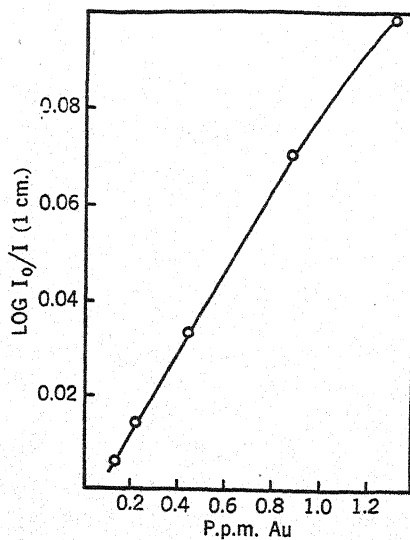


Fig. 35.—Determination of gold with *p*-diethylaminobenzylidenerhodanine according to the directions in the text (green filter, Cenco No. 2).

method for the determination of gold may be based on this behavior.<sup>12</sup> The colloidal suspension of the gold compound is quite stable. A suitable acidity for the reaction is 0.1 *N* in hydrochloric acid. The sensitivity is much decreased at higher acidities. The light absorption of the suspension becomes constant 15–20 minutes after the addition of the reagent. The reagent alone shows a very faint yellow color in acid solution. A plot of  $\log I_0/I$  against concentration gives a straight line between 0.1 and 0.9 p.p.m. of gold, which however does not pass through the origin (Fig. 35).

The most serious interference in the method is encountered from palladium which gives an even more sensitive reaction with the rhodanine reagent, so that gold must be carefully separated from palladium if there is a possibility of the latter being present. Platinum interferes less than palladium. A solution containing 0.8 p.p.m. of platinum in 0.1 *N* hydrochloric acid showed no color with the reagent after 20 minutes. Stronger solutions however give a color, especially on long standing. If silver does not exceed gold in amount, and is not present in sufficient concentration to give a precipitate of silver chloride it will not interfere seriously. A solution containing 5.5  $\gamma$  of gold and 20  $\gamma$  of silver yielded an apparent value of 6.5  $\gamma$  gold. The reaction of silver is inhibited by hydrochloric acid. Likewise, chloride inhibits the reaction of mercury with the reagent. Moreover, mercury compounds can readily be removed by gentle ignition. Neutral salts seriously disturb the determination by decreasing the color intensity.

The following procedure includes directions for the isolation of gold by coprecipitation with tellurium by addition of stannous chloride.

#### Special Solutions

*p*-Diethylaminobenzylidenerhodanine, 0.05 per cent solution in ethyl alcohol. The solution is stable.

*Stannous chloride*, 10 per cent solution of the dihydrate in 1 *N* hydrochloric acid.

*Tellurous oxide*, 0.10 per cent solution in 1 *N* hydrochloric acid.

*Aqua regia*, 1 volume of concentrated nitric acid mixed with 3 volumes of concentrated hydrochloric acid.

#### Procedure

**Isolation of Gold.**—To 25–100 ml. of solution, 1 to 2 *N* in hydrochloric acid and containing 1 to 25  $\gamma$  of gold, add 0.2 ml. of tellurous oxide solution, and, after mixing, 2 ml. of 10 per cent stannous chloride solution or more as required to reduce iron, copper, etc. and produce a brown colloidal

<sup>12</sup> The reagent has been used by B. K. Merejkovsky, *Bull. soc. chim. biol.*, **15**, 1336 (1933), for the determination of gold in biological samples. The procedure given here differs considerably from that of Merejkovsky.

suspension of tellurium. Heat to boiling and keep hot for 5–10 minutes to coagulate the precipitate. Collect the precipitate in a small porous porcelain or sintered glass filter crucible<sup>13</sup> and wash with 1:20 hydrochloric acid. Dissolve the precipitate in 1 or 2 ml. of aqua regia, wash with hot water and catch the filtrate and washings in a small (20 ml.) beaker.

Evaporate the solution to dryness on the steam bath and with the aid of a stirring rod moisten the residue with exactly 0.05 ml. of a 1:1 mixture of aqua regia and water. Then add a few milliliters of water.

**Determination of Gold.**—Add sufficient dilute hydrochloric acid to the sample solution to make its acidity 0.10 *N* after dilution to volume. Transfer the solution to a 10 or 25 ml. volumetric flask and dilute with water to about 8 or 20 ml. respectively. Add 0.20 ml. of the rhodanine solution, mix, and dilute to the mark. Obtain the transmittancy of the solution after 20 minutes, using a green filter. The standards for the reference

TABLE 37  
DETERMINATION OF GOLD WITH DIETHYLAMINO BENZYLIDENERHODANINE  
AFTER COPRECIPITATION WITH TELLURIUM

Foreign Metals	Au taken $\gamma$	Au found $\gamma$
	0.3	0.4
	5.5	5.3
	11.1	10.9
0.1 g. Fe <sup>III</sup>	11.1	10.7
0.1 g. Cu <sup>II</sup>	11.1	10.7
0.1 g. Pb	5.5	5.3

curve are best obtained by adding 0.2 ml. of tellurous oxide solution to each solution, evaporating to dryness, and treating in the same manner as the sample. It is important that the standards and the sample all have the same acidity.

If the amount of gold is very small (less than 1  $\gamma$ ) the color comparison may advantageously be made visually in tubes having a diameter less than 1 cm. In this case the final volume may be 3 to 5 ml. and no acid, other than 0.05 ml. of 1:1 aqua regia, need be added.

#### C. METHODS INVOLVING FORMATION OF STRONGLY COLORED ORGANIC COMPOUNDS BY THE OXIDIZING ACTION OF AURIC GOLD

Various organic substances are oxidized by auric salts to intensely colored products, and several methods for the determination of gold based on this principle have been described. Such methods are unspecific, for

<sup>13</sup> A small funnel with a tight plug of glass wool also serves well for the filtration.

other strong oxidizing agents will produce the same colored products, but they are nevertheless valuable in certain cases.

### 1. *o*-Tolidine Method<sup>14</sup>

Chlorauric acid converts *o*-tolidine into a yellow compound in acid solution. Interfering substances include free chlorine, osmium tetroxide, ruthenium salts, ferric iron, vanadate, tungstate, and nitrite. The sample solution, slightly acid with hydrochloric acid, is treated with a 0.1 per cent solution of *o*-tolidine in 1 *N* hydrochloric acid in the ratio of 1 ml. reagent to 25 ml. of sample, and the color comparison is made after 5 minutes against a similar standard which has been prepared at the same time. The color fades after one-half hour.

### 2. Malachite Green Method<sup>15</sup>

In faintly acid medium the leuco compound of malachite green,  $\text{Ph-CH}(\text{C}_6\text{H}_4\text{NMe}_2)_2$ , is oxidized by trivalent gold to malachite green and the originally colorless solution becomes blue-green. Iridium must be absent. Fluoride may be added to decolorize ferric iron. In brief, the determination is carried out as follows. One milliliter of reagent (0.05 g. of leuco malachite green in a mixture of 15 ml. alcohol and 35 ml. acetate buffer of *pH* 3.6) is added to the sample solution whose *pH* has been brought to 3.6 by the addition of acetate buffer, and the liquid is boiled for two minutes. After cooling, comparison is made against a similar standard with the aid of a yellow filter. When very small amounts of gold are involved, the malachite green formed can be extracted with chloroform. The author states that he was able to determine  $3 \times 10^{-6}$  per cent gold in a copper coin by the use of this method.

### 3. *o*-Dianisidine Method

Auric gold yields a red color with *o*-dianisidine in weakly acid solution, and this substance has been used as an indicator in a volumetric method for the element.<sup>3,16</sup> It may also be used for a colorimetric determination. Approximately 50 ml. of sample solution, containing only a few drops of mineral acid, are treated with 0.5 ml. of 5 per cent potassium bifluoride (buffer) and 0.1 ml. of 0.1 per cent *o*-dianisidine in 0.05 *N* hydrochloric acid. The color may be compared after 10–15 minutes. Any chlorine, bromine, or nitrosyl chloride originally present must be removed. This can be done by allowing a stream of air to impinge on the sample solution having as small a volume as possible (a few milliliters).

<sup>14</sup> W. B. Pollard, *Analyst*, **44**, 94 (1919).

<sup>15</sup> L. M. Kul'berg, *Zavodskaya Lab.*, **5**, 170 (1936).

<sup>16</sup> A. R. Jamieson and R. S. Watson, *Analyst*, **63**, 702 (1938).

The *o*-dianisidine method has been used by Block and Buchanan<sup>17</sup> in the determination of gold in biological fluids after destruction of organic matter with sulfuric acid and hydrogen peroxide, and oxidation of the gold with aqua regia.

#### D. THE MERCUROUS CHLORIDE METHOD<sup>18</sup>

When mercurous chloride is shaken with a gold solution, reduction of gold to the metal occurs on the surface of the particles and the precipitate becomes pink or purple. This behavior provides a method for determining 0.1 to 100  $\gamma$  of gold by comparison against a series of standards. Gold is reduced in strongly as well as in slightly acid solutions. Palladium likewise is reduced by mercurous chloride over a wide range of acid concentration, whereas platinum is reduced in slightly acid medium at room temperature, both metals coloring the mercurous chloride gray. Selenium and tellurium react in 6 per cent to concentrated hydrochloric acid solutions and arsenic (III) above 27 per cent acid. Iodide also colors the mercurous chloride. Oxidizing agents, including iron (III) and copper (II), interfere by preventing the precipitation of the gold. Mercurous chloride alone has a tendency to turn gray when shaken with a hydrochloric acid solution. This effect is reduced if the hydrochloric acid is first boiled with mercurous chloride and filtered.

#### ¶ Procedure

To 1–2 ml. of the sample solution, neutral or slightly acid and containing 0.1–10  $\gamma$  Au, add 5 ml. of cold 0.5 *N* hydrochloric acid previously boiled with a little mercurous chloride and filtered. Add 0.10 g. of mercurous chloride and shake in a glass-stoppered tube for 2–3 minutes. Allow the mercurous chloride to settle and compare with a series of standards similarly treated.

<sup>17</sup> W. D. Block and O. H. Buchanan, *J. Biol. Chem.*, **136**, 379 (1940).

<sup>18</sup> G. G. Pierson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 437 (1934); **11**, 86 (1939).

## CHAPTER XXI

### INDIUM

#### I. Separations

Indium (III) sulfide can be precipitated quantitatively only in weakly acid solution (acetic acid-acetate). However, it is carried down in strongly acid solution by various members of the hydrogen sulfide group, so that hydrogen sulfide precipitation of these metals should not be used as a method of separation from indium.

By precipitation with ammonium hydroxide in the presence of an ammonium salt at a  $pH$  of 5–6, indium can be separated from cadmium, nickel, cobalt, manganese, and, less successfully, from zinc and copper. Similar separations are effected by the use of sodium bisulfite, potassium cyanate,<sup>1</sup> and other reagents which bring the  $pH$  of the solution to a value at which indium hydroxide or a basic salt is precipitated. Indium hydroxide is slightly soluble in strongly basic solutions.

A method which is much used in isolating indium from ores (sphalerite, pyrite, etc.) consists in precipitation of the *metal* by addition of an excess of metallic zinc to a slightly acid solution. Lead, copper, etc. are precipitated; iron, aluminum, and gallium, among others, remain in solution. It remains to be demonstrated how good this method is for the preliminary quantitative concentration of very small quantities of indium.

Indium 8-hydroxyquinolate, like many other metal hydroxyquinolates, can be extracted with chloroform in a suitable  $pH$  range. A systematic study of the separations thus possible by adjustment of acidity, complex formation, etc. has not yet been made, but it is known that certain separations are possible (see p. 95). The possibility of separating gallium from indium by the use of 8-hydroxyquinoline has already been noted (p. 239). It seems likely that a method for separating indium from much iron can be based on the use of hydroxyquinoline, iron first being reduced to the ferrous state (see under gallium, p. 240).

#### II. Determination with 8-Hydroxyquinoline

The strong yellow color of indium 8-hydroxyquinolate in chloroform provides the basis of a colorimetric method for the determination of minute amounts of indium.<sup>2</sup> Maximum absorption is shown at *ca.* 400  $m\mu$ .

<sup>1</sup> L. Moser and F. Siegmann, *Monatsh.*, **55**, 14 (1930), make the separation of indium from cadmium, zinc, copper, nickel, and cobalt by adding an excess of potassium cyanate and boiling with potassium cyanate to precipitate indium hydroxide.

<sup>2</sup> T. Moeller, *Ind. Eng. Chem., Anal. Ed.*, **15**, 270 (1943).

Under the conditions of the procedure given below, Beer's law is obeyed up to approximately 20 p.p.m. of indium in the chloroform. The extraction of indium is complete or nearly so in the pH range 3.2–4.5 under these conditions. Below a pH of 1.0, 8-hydroxyquinoline does not enter the chloroform phase. At pH 3.5 the following metals interfere by giving a colored chloroform extract: aluminum, gallium, thallium (III), tin (II), bismuth, copper, iron (III), vanadium (V), molybdenum (VI), nickel, and cobalt (slightly). Among the metals not extracted at this pH are magnesium, calcium, strontium, zinc, cadmium, mercury (II), tin (IV), lead, manganese, chromium (III), and silver. It has been shown that indium can be determined in the presence of small quantities of zinc, lead, and cadmium.

Chloroform solutions of indium hydroxyquinolate fluoresce strongly and indium may thus be determined fluorimetrically at very low concentrations (*cf.* the method given for gallium, p. 239).

#### ¶ Procedure

Adjust the pH of the sample solution (25 ml.) to 3.5 and extract with five 5 ml. portions of 0.01 *M* solution of 8-hydroxyquinoline in chloroform. Dilute to volume (25–50 ml.) with chloroform and obtain the extinction of the solution at 400 m $\mu$ .



## CHAPTER XXII

### IRIDIUM

#### I. Separations

Iridium is precipitated as the hydrous dioxide by adding sodium bicarbonate to a boiling acid solution containing bromate until a  $pH$  of 6 is reached.<sup>1</sup> Palladium and rhodium are also precipitated, but not platinum (IV); osmium and ruthenium must be removed from the solution by volatilization of the tetroxides before the hydrolytic precipitation is made. Palladium is then precipitated as the dimethylglyoxime compound, and rhodium is precipitated with titanous chloride in the filtrate. Some iridium is carried down by the metallic rhodium, and the precipitate must be dissolved in hot concentrated sulfuric acid and the precipitation repeated. Iridium is thus left with titanium which is precipitated with cupferron (double precipitation is necessary). The organic matter in the filtrate is destroyed with nitric and sulfuric acids. The procedure described has been used only on the macro scale and it is not known how well it will work when very low concentrations of iridium and the other metals must be dealt with. The addition of a little ferric iron should help to gather iridium in the hydrous oxide precipitation, the ionic radii of iron (III) and iridium (IV) being very similar (p. 23).

#### II. Methods of Determination

The direct colorimetric methods for iridium are not as sensitive as would be desired. The strong red-brown color of  $\text{IrCl}_6^-$  allows moderately low concentrations of iridium to be determined. The sensitivity is in the neighborhood of  $2 \gamma$  Ir per  $\text{cm}^2$ . Trivalent iridium can be oxidized to the quadrivalent state with a slight excess of chlorine water. The color intensity is the same in 0.1 and 2  $N$  hydrochloric acid. Possibly the interference of platinum and rhodium can be circumvented by determining the transmittancy of the solution before and after the addition of a suitable reducing agent which will convert  $\text{IrCl}_6^-$  into the much less strongly colored chloroiridite ion without affecting the chloro complexes of the other metals.

A characteristic color reaction for iridium may be obtained by evaporating the solution to fumes with sulfuric acid and adding nitric acid or potassium periodate and again heating. A blue color is produced which becomes violet when the solution is diluted with nitric acid (water destroys the

<sup>1</sup> R. Gilchrist, *Bur. Standards J. Research*, **12**, 291 (1934); **9**, 547 (1932). R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

color). A similar color is obtained when an iridium solution is evaporated to fumes with perchloric acid. Unfortunately this reaction is not very sensitive, no more so than the chloroiridate test.

The indirect colorimetric determination of iridium rests on the rather strong oxidizing power of chloroiridate ion, which is thus able to convert various organic compounds into strongly colored products. Two reagents which have been used are benzidine<sup>2</sup> and leuco-malachite green.<sup>3</sup> Khlopin carries out the determination by adding 0.10 ml. of benzidine solution (1 g. benzidine dissolved in 10 ml. of glacial acetic acid and diluted to 50 ml. with water) to 10 ml. of very nearly neutral sample solution of chloroiridate (5  $\gamma$  or more Ir) and comparing the blue color against standards having the same composition as the sample.

<sup>2</sup> V. G. Khlopin, *Ann. inst. platine*, **1**, 324 (1926).

<sup>3</sup> See p. 255.

## CHAPTER XXIII

### IRON

#### I. Separations

A special study of the isolation of minute quantities of iron, with special reference to the determination of iron in reagent chemicals, was made by Stokes and Cain.<sup>1</sup> These authors separate ferric iron as the hydroxide with hydrous manganese dioxide<sup>2</sup> as collector, and as the sulfide with cadmium sulfide as collector. Precipitation of iron as hydroxide may be applied in its isolation from solutions of the alkalis and alkaline earth metals, zinc, lead, cadmium, and other metals whose hydroxides are precipitated at a higher pH than ferric hydroxide or which can be kept in solution by an excess of ammonium hydroxide. Phosphate does not prevent complete precipitation of iron. The method cannot be used in the presence of tartrate, citrate, oxalate, pyrophosphate, arsenate, arsenite, or organic matter in general, which may prevent complete precipitation of ferric hydroxide. When such substances are present, iron is precipitated with ammonium sulfide in the presence of a little cadmium.<sup>3</sup> This method is limited to samples free from appreciable amounts of metals giving slightly soluble sulfides, except those soluble in excess ammonium sulfide. Directions for these procedures are given on p. 269.

Precipitation of iron with ammonium sulfide in the presence of tartrate serves to separate it from titanium, uranium, vanadium, phosphate, and some other elements less likely to interfere in the colorimetric determination.

Precipitation of iron by cupferron and neo-cupferron in acid medium is of importance as a separation from chromium, cobalt, nickel, manganese and a number of other elements which may prove disturbing in some of the colorimetric methods. Ferric cupferrate can be extracted with a number of organic solvents (ether and chloroform).<sup>4</sup>

<sup>1</sup> H. N. Stokes and J. R. Cain, *J. Am. Chem. Soc.*, **29**, 409, 443 (1907).

<sup>2</sup> This collector was used instead of aluminum hydroxide because the colorimetric procedure employed by the authors mentioned called for solution of the precipitate in thiocyanic acid in which aluminum hydroxide cannot be dissolved completely. It may also be pointed out that the manganese precipitate can be used to gather iron when sodium hydroxide is used for precipitation.

<sup>3</sup> For the determination of iron in sea water after precipitation with ammonium sulfide with basic magnesium salts as collector, see N. W. Rakestraw, H. E. Mahneke, and E. F. Beach, *Ind. Eng. Chem., Anal. Ed.*, **8**, 136 (1936).

<sup>4</sup> R. Paulais, *Compt. rend.*, **206**, 783 (1938). Cf. S. M. Berman, J. J. Chap, and D. M. Taylor, *J. Assoc. Official Agr. Chem.*, **20**, 635 (1937).

Extraction of ferric 8-hydroxyquinolate with chloroform from an acetic acid-acetate medium is occasionally of value in isolating traces of iron.

Iron in the ferrous state can be extracted by shaking a solution of pH 8 to 9 with a chloroform solution of isonitrosoacetophenone.<sup>5</sup> Many other heavy metals also form chloroform-soluble complexes with the reagent. The ferrous complex has a green color in chloroform and a sensitive colorimetric method for iron can be based on this property.

## II. Methods of Determination

There is no lack of colorimetric reagents for iron, but comparatively few are well suited for the determination of traces of iron. Some reagents react with ferric iron, others with ferrous. The former generally have the dis-

TABLE 38  
PROPERTIES OF SOME REAGENTS FOR THE COLORIMETRIC DETERMINATION OF IRON<sup>a</sup>

Reagent	Sensitivity <sup>b</sup> γ Fe/cm. <sup>2</sup>	Stability of color	pH range	Effect of excess reagent	Beer's Law
α,α'-Bipyridyl	0.007 (522 mμ)	1 year	3-9	None	Obedied
2,2',2''-Terpyridyl	0.005 (552 mμ)	1 year	3-10	None	Obedied
Ferron	0.015 (610 mμ)	1-2 weeks	2.7-3.1	Change in hue	Not obeyed
Mercaptoacetic acid	0.014 (540 mμ)	Several hours	7-12	None	Obedied
o-Phenanthroline	0.005 (508 mμ)	6 months or more	2-9	None	Obedied
Salicylaldoxime	0.011 (480 mμ)	1 day	6.2-6.6	None	Obedied
Salicylic acid	0.03 (520 mμ)	2-3 days	2.5-2.7	Increases inten- sity	Obedied
Thiocyanate	0.008 (480 mμ)	Fades rapidly	0.05->1 N	Increases inten- sity	Slight devia- tion
Thiocyanate and acetone	0.004 (480 mμ)	Fades	0.05->1 N	Increases inten- sity	Slight devia- tion

<sup>a</sup> This table is based mostly on data given by J. T. Woods and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 554 (1941).

<sup>b</sup> Number of micrograms of iron in a column of solution of 1 cm.<sup>2</sup> cross section giving an extinction of 0.001.

advantage that they cannot be used in the presence of appreciable concentrations of such ions as fluoride and pyrophosphate which form stable complexes with trivalent iron in acid medium, in which the color reaction must be carried out. In such cases better results can frequently be obtained by resorting to a reagent reacting with ferrous iron, which does not form such complexes or at least less stable ones.

Some characteristics of common colorimetric reagents for iron are given in Table 38. For the most accurate determination of minute amounts of iron, the use of o-phenanthroline (or the similar reagent α,α'-bipyridyl) is recommended. It reacts with ferrous iron. In its use, account must be

<sup>5</sup> F. Kröhnke, *Ber.*, **60**, 527 (1927); E. Abrahamczik, *Mikrochemie ver. Mikrochim. Acta*, **25**, 240 (1938).

taken of the possible interference of copper, nickel, and cobalt, which also react in very low concentrations. Thiocyanate is quite useful at times, but suffers from the disadvantage of giving a product whose color fades rather rapidly. Reagents which require adjustment of the pH within a narrow range are obviously not very desirable, and those that require a neutral or basic medium for reaction are of limited practical value.

#### A. THE THIOCYANATE METHOD<sup>6</sup>

Thiocyanate is still extensively used for the determination of iron even though other reagents give better results. In spite of its limitations, the thiocyanate method is a serviceable one. The reagent is cheap and readily available, and has the advantage over other reagents that it can be used in rather strongly acid solution.

The formula of the substance formed when ferric iron reacts with thiocyanate is uncertain. The reaction is a complex one and apparently more than one product can be obtained depending on conditions. Evidence points to the formation of an ion such as  $\text{Fe}(\text{CNS})^{++}$  or  $\text{Fe}(\text{CNS})_2^+$  in the color reaction.<sup>7</sup> From the quantitative standpoint the reaction is a delicate one, because the color intensity depends upon a number of factors such as the excess of thiocyanate, the kind of acid present, the time of standing, etc.

A relatively large excess of thiocyanate is desirable. Not only is the sensitivity increased by increasing the thiocyanate concentration, but the color intensity then remains more nearly constant when the acidity is varied. Moreover a high concentration of thiocyanate reduces the errors due to chloride, phosphate, and other ions forming complexes with ferric iron in acid solution. A final concentration of thiocyanate of about 0.3 M is generally satisfactory. Care must be taken to have the same concentration of thiocyanate in the unknown and the standard, because a relatively small difference leads to a fairly large change in color intensity. Metals such as cadmium and mercury which form complexes with thiocyanate bleach the iron color and the effect can be overcome only partially by adding more thiocyanate when these metals are present in fair amounts.

The acidity of the solution plays a minor role in determining the color strength provided enough acid is present to prevent appreciable hydrolysis of the iron, and the acid does not form a complex with ferric iron. Thus when nitric acid is used for acidification the color intensity is virtually constant in the range 0.05 to 0.8 N. Even with hydrochloric acid the

<sup>6</sup> J. T. Woods and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 551 (1941); C. A. Peters and C. L. French, *ibid.*, **13**, 604 (1941).

<sup>7</sup> H. E. Bent and C. L. French, *J. Am. Chem. Soc.*, **63**, 568 (1941); M. Møller, *Kem. Maanedssblad*, **18**, 138 (1937), *Chem. Abstracts*, **33**, 9179 (1939).

color intensity is but slightly lower in 1 *N* than in 0.1 *N* solution when the solution is 0.3 *M* in thiocyanate (Fig. 36). Moreover in 0.1 *N* hydrochloric acid solution the color strength is the same as in nitric acid solution. Sulfuric acid reduces the color intensity in accordance with expectations. In order to avoid error, the same amount of sulfuric acid must be present in both unknown and standard.

The ferric-thiocyanate system does not in general<sup>8</sup> follow Beer's law. The color intensity does not increase quite proportionately with the iron concentration (Fig. 36). The magnitude of the resulting error can be seen from the figure. In 0.5 *N* nitric acid, with a standard containing 4 p.p.m. of iron the error is +3.5 per cent for an unknown containing 2 p.p.m. of

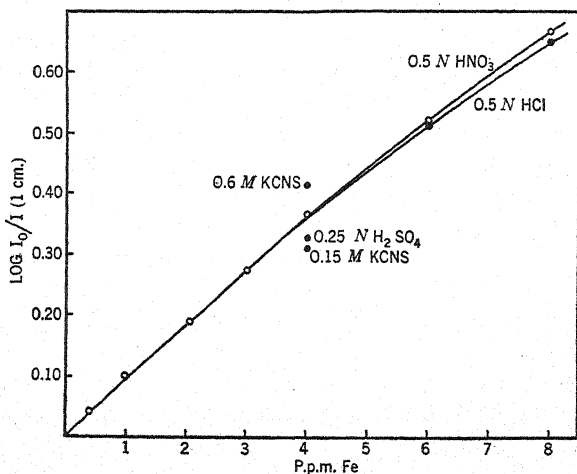


Fig. 36.—Determination of iron by the thiocyanate method (green filter). All solutions, except as indicated, 0.3 *M* in KCNS. Curve for 0.1 *N* HCl solutions is practically coincident with 0.5 *N* HNO<sub>3</sub> curve.

iron and *ca.* -6 per cent for 6 p.p.m. of iron (green filter used). The error is larger in hydrochloric acid solution. The avoidance of the error due to the failure of Beer's law entails the use of a standard having about the same iron concentration as the unknown or the construction of a reference curve.

Another source of error in the method arises from the fading of the ferric thiocyanate color when the solution is exposed to light, because of the reduction of ferric iron by thiocyanate or its decomposition products. In diffuse daylight a solution containing 4 p.p.m. of iron in 0.5 *N* HCl and 0.3 *M* thiocyanate showed approximately a 10 per cent decrease in color intensity after 10 minutes. The fading appears to be somewhat slower at lower

<sup>8</sup> According to Woods and Mellon,<sup>6</sup> Beer's law is obeyed up to 10 p.p.m. of iron in hydrochloric acid solution of pH 1.5-1.65.

acidities. At least in the initial stage, the fading is directly proportional to the time (Fig. 37). In 0.5 *N* nitric acid solution the fading ceases after about fifteen minutes and the color intensity then increases, eventually becoming stronger than it was originally. This behavior is due to a reaction between the nitric acid and thiocyanate which results in the formation of a yellow-brown product. In the absence of iron this reaction becomes evident only after an hour or so in diffuse daylight.<sup>9</sup>

TABLE 39  
DETERMINATION OF IRON WITH THIOCYANATE

Concentration Fe p.p.m.	Acid concentration	Extinction (1 cm. cell, green filter)
4.0	0.05 <i>N</i> HNO <sub>3</sub>	0.358
4.0	0.2 <i>N</i> HNO <sub>3</sub>	0.358
4.0	0.5 <i>N</i> HNO <sub>3</sub>	0.367
4.0	0.8 <i>N</i> HNO <sub>3</sub>	0.364
0.4	0.5 <i>N</i> HNO <sub>3</sub>	0.041
1.0	0.5 <i>N</i> HNO <sub>3</sub>	0.100
2.0	0.5 <i>N</i> HNO <sub>3</sub>	0.190
3.0	0.5 <i>N</i> HNO <sub>3</sub>	0.275
6.0	0.5 <i>N</i> HNO <sub>3</sub>	0.520
8.0	0.5 <i>N</i> HNO <sub>3</sub>	0.666
4.0	0.1 <i>N</i> HCl	0.368
4.0	0.5 <i>N</i> HCl	0.360
4.0	0.8 <i>N</i> HCl	0.356
4.0	1.0 <i>N</i> HCl	0.358
2.0	0.1 <i>N</i> HCl	0.193
6.0	0.1 <i>N</i> HCl	0.520
8.0	0.1 <i>N</i> HCl	0.663
2.0	0.5 <i>N</i> HCl	0.186
6.0	0.5 <i>N</i> HCl	0.511
8.0	0.5 <i>N</i> HCl	0.648
4.0	0.25 <i>N</i> H <sub>2</sub> SO <sub>4</sub>	0.328

The following ions especially interfere in the determination:

1. Fluoride, metaphosphate, pyrophosphate,<sup>10</sup> oxalate, etc. which form complexes with ferric iron in acid solution. Sulfate and phosphate

<sup>9</sup> The fading of the ferric thiocyanate color may be much decreased by adding certain oxidizing agents in regulated amount. Hydrogen peroxide is recommended for the purpose by C. A. Peters, M. M. MacMasters, and C. L. French, *Ind. Eng. Chem., Anal. Ed.*, 11, 502 (1939), who make the 0.01 *N* hydrochloric acid solution 0.001–0.003 *M* in H<sub>2</sub>O<sub>2</sub>. More hydrogen peroxide than this produces a yellow color with thiocyanate, especially if the solution is acid.

<sup>10</sup> The interference of metaphosphate and pyrophosphate can be prevented or greatly reduced by adding aluminum (as nitrate) to form stable complexes, according

interfere if present in appreciable amounts. As much as 500 p.p.m. of  $P_2O_5$  as orthophosphate may be present without producing any serious error.

2. Silver and mercurous mercury which yield insoluble thiocyanates.
3. Copper, bismuth, ruthenium, osmium, and molybdate which may yield colors with thiocyanate. Manganese should not be present in large amounts.
4. Mercury (II), cadmium, zinc, and antimony (III), which form complexes with thiocyanate and reduce the intensity of the iron-thiocyanate color.

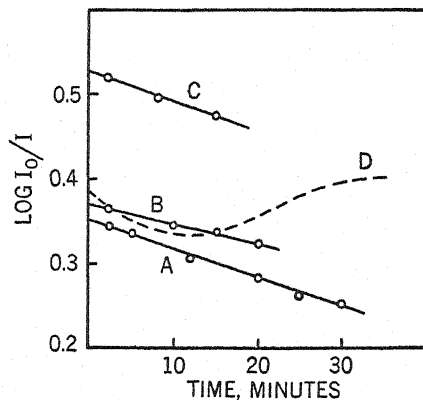


Fig. 37.—Effect of time on ferric thiocyanate color intensity. Solutions exposed to diffuse daylight; strength of light only approximately the same in the different experiments, so that curves are only roughly comparable. A. 4 p.p.m. Fe in 0.5  $N$   $HCl$ . B. 4 p.p.m. Fe in 0.1  $N$   $HCl$ . C. 6 p.p.m. Fe in 0.1  $N$   $HCl$ . D. 4 p.p.m. Fe in 0.2  $N$   $HNO_3$ .

Addition of a miscible organic solvent having a low dielectric constant intensifies the iron thiocyanate color. Acetone<sup>11</sup> and 2-methoxyethanol ("methyl cellosolve")<sup>12</sup> have been recommended for the purpose. In 60 per cent acetone solution the color is about twice as strong as in water. It

to H. E. Wirth, *Ind. Eng. Chem., Anal. Ed.*, **14**, 724 (1942). It may be mentioned that Wirth found the interference of pyrophosphate and phosphate to be greater in solutions of  $pH$  1 (and higher) than in those of  $pH$  0.5 or less; metaphosphate interfered seriously even in strongly acid solutions. Vanossi (see reference on p. 267) has also used aluminum to prevent the interference of complex phosphates and fluoride.

<sup>11</sup> See for example W. Marriott and C. G. Wolf, *J. Biol. Chem.*, **1**, 451 (1906); J. T. Woods and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 551 (1941).

<sup>12</sup> H. W. Winsor, *Ind. Eng. Chem., Anal. Ed.*, **9**, 452 (1937). A solution of thiocyanate in water plus 2-methoxyethanol soon turns yellow on exposure to light whereas the acetone solution is not appreciably changed.



has been shown that there is less interference from such ions as fluoride and oxalate in a water-acetone solution than in water alone. Thus Woods and Mellon found that in order to keep the error below 2 per cent not more than 30 and 0 p.p.m. of  $F^-$  and  $C_2O_4^{2-}$  could be present in water solution, whereas the limits of the same ions were 400 and 30 p.p.m. in 60 per cent acetone solution. The rate of fading of the iron color is lower in acetone solution than in water. General use of acetone to increase the sensitivity (with certain methods of observation) and color stability is not possible because of the slight solubility of many salts in acetone-water mixtures. Moreover cobalt gives an intense blue color with thiocyanate in the presence of acetone (p. 202).

The ferric thiocyanate complex may be extracted from aqueous solution by amyl alcohol, a mixture of amyl alcohol and ether,<sup>13</sup> a mixture of the monobutyl ether of ethylene glycol and ethyl ether,<sup>14</sup> ethyl acetate,<sup>15</sup> etc. Extraction by an immiscible solvent is of some importance when traces of iron are to be determined. The extraction may be carried out by shaking in glass-stoppered tubes, and the colors of the upper layers compared by viewing the sample and standard tubes sideways. Although great sensitivity can thus be obtained, the relatively rapid discoloration of the organic solvent layer is an objection to the method. The upper layer soon turns yellow, especially if the aqueous layer is relatively acid.

Iron may be oxidized to the ferric condition by the addition of a slight excess of potassium permanganate to the acid solution. The excess permanganate is quickly reduced in acid solution by thiocyanate and no colored products are formed.

Immediately following are general directions for determining iron with thiocyanate. Directions for determining very small amounts of iron after isolation by precipitation as the hydroxide and sulfide are then given on p. 269.

### Reagents

*Potassium thiocyanate*, 1.5 M or other convenient concentration. A good grade of reagent may generally be used without purification. The salt may be tested for iron by adding a milliliter or two of acetone to 1-2 g.; the solution should show no color. If purification seems desirable, add a few milligrams of an aluminum salt to the solution, precipitate aluminum hydroxide with a few drops of ammonia, and filter off the precipitate which will contain the iron.

*Hydrochloric or nitric acid*. Except in the determination of extremely small amounts of iron, the best grade of acid may be used without purification. If purification is necessary, distil in all-Pyrex apparatus and store the acid in Pyrex or other

<sup>13</sup> H. N. Stokes and J. R. Cain, *J. Am. Chem. Soc.*, **29**, 409 (1907).

<sup>14</sup> A. Bernhard and I. J. Dekter, *Science*, **75**, 517 (1932).

<sup>15</sup> R. Vanossi, *Anales soc. quim. argentina*, **29**, 48 (1941).

resistant glass. Any oxides of nitrogen in nitric acid should be removed by drawing filtered air through the diluted acid.

*Acetone.* The reagent quality product may be used without purification.

*Amyl alcohol and ethyl ether* (for the extraction procedure). Shake each liquid with two or three portions of water of equal volume, and then mix in the volume ratio 2 alcohol to 1 ether.

*Standard iron solution*, 0.100 mg. Fe per ml. Dissolve 0.1000 g. electrolytic iron or iron wire for standardization in 50 ml. of 1:3 nitric acid, boil to expel oxides of nitrogen, and dilute to 1 liter with iron-free water. If desired, more dilute solutions can be prepared from this solution by diluting with 0.2 *N* nitric acid.

## ¶ General Procedure

**Ordinary Procedure.**—The sample solution may conveniently contain up to 10 p.p.m. of Fe (III) after final dilution to volume if a photoelectric photometer with a 1 cm. cell is used, and up to 20 p.p.m. of iron if a Duboscq colorimeter is employed. The acidity may vary from 0.05 to 1 *N* in nitric or hydrochloric acid.

Add sufficient thiocyanate, accurately measured, to make the final concentration about 0.3 *M*, dilute to volume with water, and determine the transmittancy of the mixed solution *at once*. Use a filter showing maximum transmission at or near 480 m $\mu$ . The standard series method may also be used, but the colorimetric titration technique should be avoided.

The standard iron solutions used in the construction of the reference curve should contain approximately the same amount and kind of acid as the unknown, especially if hydrochloric acid is used for acidifying. The concentration of thiocyanate must be the same in the standards and unknown. If sulfuric acid is present in the sample an equal amount must be added to the standards.

**Procedure with Acetone.**—In the absence of precipitable salts, the use of acetone to increase the intensity of the color and its stability may be advantageous. The acidity of the sample solution and thiocyanate concentration may be the same as before. Add sufficient acetone, exactly measured, to give a 50 to 60 per cent solution by volume, make up to volume, and obtain the transmittancy without undue delay. The standards must have the same composition as the sample solution. Use the same filter as above.

**Extraction with an Immiscible Organic Solvent.**—The solution may conveniently have a volume of 10 ml. and may contain less than 1  $\gamma$  of ferric iron (as little as 0.1  $\gamma$  will give an easily visible color). The acidity should be as low as practicable. Transfer the solution to a 1.8  $\times$  15 cm. glass-stoppered tube and prepare a series of standards of the same composition as the unknown. The volume of all the solutions must be the same. Add to each tube sufficient thiocyanate to make its concentration 0.3 *M*, and

2.0 to 3.0 ml. of a 2:1 volume mixture of amyl alcohol and ethyl ether (or a 1:1 mixture of monobutyl ether of ethylene glycol and ethyl ether). Immediately shake the tubes vigorously for about ten seconds, allow the phases to separate, and compare the colors by viewing the tubes sideways against a white background. If the colors are too strong for good comparison dilute with more of the organic solvent.

If a photometer is to be used, the volume of the organic solvent may have to be increased. The wave length for maximum absorption in amyl alcohol-ether is approximately 500  $m\mu$ .

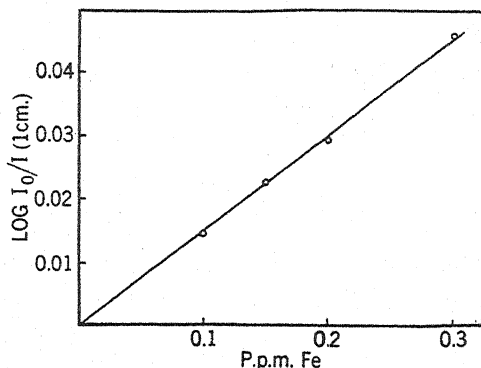


Fig. 38.—Determination of low concentrations of iron by the thiocyanate-acetone method (green filter). 50 per cent by volume of acetone (p. 270).

#### Determination of Traces of Iron with Thiocyanate after Precipitation as Hydroxide and Sulfide

In the procedure given below, traces of iron are coprecipitated with hydrous manganese dioxide or cadmium sulfide according to the method of Stokes and Cain (*loc. cit.*) and finally determined with thiocyanate in acetone medium to increase the sensitivity and the stability of the color. It is of course possible to determine iron by any other sensitive method after its isolation, account being taken of the possible effect of the coprecipitating agent and other extraneous substances.

#### Reagents

**Hydrochloric acid.** If only a small amount of hydrochloric acid is needed in preparing the sample for analysis, the analytical reagent may be used without purification, but if a large volume is required the acid should be distilled in Pyrex, or still better, hydrogen chloride obtained by dropping sulfuric acid into hydrochloric acid should be absorbed in redistilled water.

**Ammonium hydroxide.** Pass pure ammonia into water, or distil concentrated ammonium hydroxide. Keep the solution in a ceresin-coated bottle.

*Potassium permanganate*, 0.5 per cent aqueous solution.

*Cadmium chloride or sulfate*, 0.1 *M* aqueous solution. If removal of traces of iron in the salt is considered advisable, use the manganese dioxide method described in the procedure below.

*Sodium potassium tartrate*, 20 per cent. Remove iron as sulfide with cadmium sulfide as collector (see procedure below).

*Ammonium sulfide solution*. Prepare from pure hydrogen sulfide (not from ferrous sulfide + acid) and pure ammonia.

*Thiocyanate reagent*. To 20 ml. of 1.5 *M* potassium thiocyanate and 8 ml. of 1:1 hydrochloric acid add 50 ml. of reagent-grade acetone and dilute to 100 ml. with water.

*Ethyl alcohol*.

## ¶ Procedure

**Preparation of Sample.**—Acids such as hydrochloric, nitric, sulfuric, etc. should be evaporated nearly to dryness in fused silica (not in platinum which invariably contains iron extracted by acid), with provision for exclusion of dust and prevention of dripping back of condensed liquid into the container. There is no loss of iron in the evaporation of hydrochloric acid.

Ammonia should be evaporated nearly to dryness in silica or platinum.

Salts should, in general, be dissolved in water acidified with hydrochloric acid. As much as 10–20 g. of solid may be taken.

**Precipitation of Iron as Hydroxide with Hydrated Manganese Dioxide as Collector.**—The solution may conveniently have a volume of 50 or 100 ml., although larger volumes may be used, and if possible at least 1  $\gamma$  iron should be present. The equivalent of at least 1 ml. of 1:1 hydrochloric acid should be present. For each 100 ml., add 0.5 ml. of potassium permanganate solution and sufficient ammonium hydroxide to give a distinct odor, followed by 1 ml. of ethyl alcohol. If metals such as zinc, lead, etc. are present in large amounts, add only enough ammonia to give a very slight permanent precipitate. Heat to boiling and keep near the boiling point until the precipitate of  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  has coagulated well.

Collect the precipitate on a small loose-textured filter paper (5 cm. diameter) which previously has been washed with warm dilute hydrochloric acid and then with water. Wash the precipitate with a few portions of water, and then with a few milliliters of acetone, which first has been poured into the precipitation vessel to remove water. Shake out any acetone in the stem of the funnel and allow most of the acetone in the paper and precipitate to evaporate. Pour 5 ml. of thiocyanate reagent into the cold precipitation vessel to dissolve any precipitate on its walls and transfer the solution to the filter paper. Catch the solution in a dry 10 ml. volumetric flask and wash the paper with more of the reagent, finally making the volume up to the mark with the reagent. If these operations are carried out without undue delay there will be no important loss of acetone by evaporation from the solution.

Immediately obtain the transmittancy of the solution, using a suitable filter (p. 268). The calibration curve is constructed by pipetting 0.10, 0.20, and 0.30 ml. of 0.001 or 0.002 per cent iron solution (prepared by diluting a stronger solution, p. 268) into a dry 10 ml. volumetric flask, diluting to volume with the acetone reagent solution, and determining the transmittancy. The effect of the water introduced through the iron solution may be disregarded. A blank must be run to find the amount of iron in the reagents.

**Precipitation of Iron as Sulfide with Cadmium Sulfide as Collector.**—

To the neutral or only slightly acid solution, which has been treated with sufficient pure sodium potassium tartrate if aluminum, chromium, etc. are present, add 1 ml. of cadmium solution and a slight excess of ammonium sulfide (or enough to dissolve any sulfides soluble in excess reagent). Allow the mixture to stand for one-half to one hour with occasional stirring. Collect the precipitate on a small washed paper filter and wash with water to which a little ammonium sulfide has been added. Dissolve the precipitate in warm 1:1 hydrochloric acid and return the solution to the precipitation vessel. Boil out hydrogen sulfide and precipitate iron as hydroxide with manganese dioxide collector as described above.

If the original solution contained tartrate, oxalate, etc., dissolve the precipitate in warm dilute nitric acid, add potassium permanganate solution in excess and heat the solution until any organic matter has been decomposed.

**B. THE *o*-PHENANTHROLINE METHOD<sup>16</sup>**

A good sensitive method for the determination of iron is based on the formation of an orange-red complex,  $[(C_{12}H_8N_2)_3Fe]^{++}$ , between *o*-phenanthroline and ferrous iron. The color intensity is independent of the acidity in the pH range 2–9; below pH 2 the color develops slowly and is much weaker. The complex is very stable and solutions show no change in color after many months. Beer's law is closely followed.

Ferric iron may be reduced with hydroxylamine hydrochloride or hydroquinone.

Aside from colored ions, the following interfere to a greater or less extent.<sup>17</sup> Silver and bismuth give precipitates. Certain divalent metals such as cadmium, mercury, and zinc form slightly soluble complexes with the reagent and, moreover, reduce the intensity of the iron color, but the interference can be diminished by adding a larger excess of reagent. The maximum permissible concentration of these ions for 2 p.p.m. of iron is

<sup>16</sup> W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1938); A. Thiel, H. Heinrich, and E. van Hengel, *Ber.*, **71B**, 756 (1938); L. G. Saywell and B. B. Cunningham, *Ind. Eng. Chem., Anal. Ed.*, **9**, 67 (1937).

<sup>17</sup> Fortune and Mellon, *loc. cit.*

approximately 50 p.p.m. of Cd, 1 p.p.m. of Hg and 10 p.p.m. of Zn. Mercury (I) may be present up to 10 p.p.m. (pH 3-9). Beryllium (50 p.p.m.) does not interfere if the pH lies between 3.0 and 5.5; below the former pH a stable complex is formed with the reagent and above the latter pH the hydroxide is precipitated. Molybdenum (VI) does not interfere above pH 5.5 but in more acid solutions it gives a turbidity. Tungstate decreases the color intensity but 5 p.p.m. of W does no harm. Copper may not exceed 10 p.p.m. and in the presence of this element the pH must lie between 2.5 and 4.0. Nickel interferes by producing a change in hue and raising the transmittancy below 540 m $\mu$ , so that no more than 2 p.p.m. may be present. Cobalt gives a yellow color and should not exceed 10 p.p.m. at pH 3-5. Tin (II) should not exceed 20 p.p.m. for pH 2-3, and tin (IV) should not be above 50 p.p.m. (pH 2.5).

If the pH is kept above 6 and 3 respectively, oxalate and tartrate in concentrations as high as 500 p.p.m. do not interfere. In the presence of pyrophosphate the pH must be above 6; then 50 p.p.m. of  $\text{P}_2\text{O}_7^{4-}$  causes an error of only 1 per cent with 2 p.p.m. of iron.<sup>18</sup> Phosphate may be present up to 20 p.p.m. of  $\text{P}_2\text{O}_5$  (pH 2-9). Fluoride (500 p.p.m.) does not interfere if the pH is kept above 4.0. Chloride and sulfate are without effect, at least in moderate amounts. If perchlorate is present in more than small amounts, a precipitate of the slightly soluble *o*-phenanthroline perchlorate may be produced.

A great advantage in the use of *o*-phenanthroline lies in the possibility of using it in slightly acid solutions, so that hydroxides, phosphates, etc. of many metals are not precipitated.

$\alpha, \alpha'$ - (or 2,2')-Bipyridyl and 2,2',2''-Terpyridyl.<sup>19</sup>—These reagents are very similar to *o*-phenanthroline, and may be used in place of it, but for general use have no advantages. Terpyridyl has the disadvantage of being very sensitive to cobalt and copper, and nearly as much so to nickel.

#### Special Solutions

*Hydroquinone*, 1 per cent solution in sodium acetate-acetic acid buffer of pH *ca.* 4.5 (mix 65 ml. of 0.1 *M* acetic acid and 35 ml. of 0.1 *M* sodium acetate). Keep the solution in an icebox and discard when a coloration appears.

*Sodium acetate*. 2 *M* and 0.2 *M* solutions are convenient concentrations.

*o*-Phenanthroline, 0.5 per cent solution of the monohydrate in water. Warm to effect solution.

<sup>18</sup> F. C. Hummel and H. H. Willard, *Ind. Eng. Chem., Anal. Ed.*, **10**, 14 (1938), found that as much as 50 mg. of P as pyrophosphate in 25 ml. of solution of pH 3.5 did not interfere in the determination of 0.2 mg. of iron if the mixture was allowed to stand at least one-half hour after the addition of *o*-phenanthroline and reducer (hydroquinone).

<sup>19</sup> M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **14**, 862 (1942). This paper contains further references on the use of these reagents.

### ¶ Procedure<sup>20</sup>

Take an aliquot portion of the sample, only slightly acid, containing 0.2–0.5 mg. of iron (Duboseq colorimeter) or 0.01–0.2 mg. (photometer, 1 cm. cell) and transfer to a 25 ml. volumetric flask. Determine by the use of a similar aliquot portion containing a few drops of bromphenol blue the volume of sodium acetate required to bring the pH to 3.5. Add the same volume of acetate to the working aliquot and then 1 ml. each of hydroquinone and *o*-phenanthroline solutions. Allow to stand for an hour to assure complete reduction of iron, make up to volume with water, and determine the transmittancy of the solution, using a filter showing maximum transmission at 480–520 m $\mu$ . If a colorimeter is used, compare against a standard containing about the same iron concentration as the sample solution. For possible interference from aluminum and phosphate, see footnote 47.

**Note.**—An alternative procedure with hydroxylamine hydrochloride as reducing reagent is the following. Adjust the pH of the slightly acid solution to 3–6 with sodium acetate solution after the addition of 1 ml. of 10 per cent hydroxylamine hydrochloride. Add 1 ml. of *o*-phenanthroline (0.5 per cent), mix, dilute to the mark, and obtain the transmittancy of the solution after 5 or 10 minutes (or after 1 hour if much pyrophosphate is present). The standards should be treated in the same manner, and should preferably have the same final pH as the sample solution.

### C. MERCAPTOACETATE (THIOGLYCOLATE) METHOD<sup>21</sup>

In ammoniacal medium, mercaptoacetate (as the ammonium salt HS·CH<sub>2</sub>COONH<sub>4</sub>) reacts with iron to yield a soluble red-purple product. The color is a function of the total iron present, both ferrous and ferric iron reacting. The reaction must be carried out in basic medium and this is one disadvantage of the method. Moreover a number of metals, including cobalt, nickel, lead, bismuth, mercury (I), uranium (UO<sub>2</sub><sup>++</sup>), silver and gold produce colors, more or less strong, with the reagent. The colors due to cobalt (yellow-red) and uranyl (orange) ions are very strong. Manganese gives an amber color if the solution is shaken or stirred (air-oxidation) but the color fades in a few minutes and as much as 100 p.p.m. of the element does not interfere. Certain metals, among them copper, arsenic (III), tin (II), zinc, and cadmium bleach the iron color, although this effect can be diminished by the addition of more reagent. Very high concentrations of salts of the alkali metals decrease the color intensity somewhat. On the other hand, anions have but a slight effect on the color. As much as 5000 p.p.m. of chloride, fluoride, orthophosphate, tartrate, oxalate, citrate,

<sup>20</sup> F. C. Hummel and H. H. Willard, *Ind. Eng. Chem., Anal. Ed.*, **10**, 14 (1938).

<sup>21</sup> H. W. Swank and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 7 (1938); E. Lyons, *J. Am. Chem. Soc.*, **49**, 1916 (1927).

and acetate ion do not interfere. Pyrophosphate in a concentration of 5000 p.p.m. of  $P_2O_5$  causes an error of -8 per cent with 1 p.p.m. of iron. Nitrous acid and cyanide must be absent. Molybdate gives a yellow color in relatively high concentrations. Tungsten (> 20 p.p.m.) as tungstate yields a blue color with the reagent.

Beer's law is closely followed by the color system and the color intensity is independent of the exact concentration of the reagent and the pH in the range 6-11. The color is fairly stable (at least 6 hours in diffuse light and 12 hours or more in the dark). Shaking tends to restore the color of a faded solution (air-oxidation).

### ¶ Procedure

Add 2 ml. of ammonium mercaptoacetate (neutralize a 10 per cent by volume solution of mercaptoacetic acid with ammonium hydroxide) and then 10 ml. of 3 or 4 M ammonia to the approximately neutral solution and dilute to 100 ml. with water. Compare with a similar standard in any convenient way or measure the transmittancy.

The final concentration of the solution may conveniently be 0.05-0.2 mg. Fe in 100 ml. Maximum absorption is shown by the solution at wave lengths 530-540 m $\mu$ . It is advisable to measure or compare the color soon after it has been developed.

### D. OTHER METHODS

Among other reagents that have been used for the determination of iron, the following may be mentioned: thiosalicylic acid,<sup>22</sup> salicylic acid,<sup>23</sup> salicylaldehyde,<sup>24</sup> ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid),<sup>25</sup> 8-hydroxyquinoline-5-sulfonic acid,<sup>26</sup> 8-hydroxyquinoline,<sup>27</sup> acetyl acetone,<sup>28</sup> gallic acid, pyrocatechol<sup>29</sup> pyrazolone,<sup>30</sup> alloxantin,<sup>31</sup> nitroso R salt,<sup>32</sup> cupferron,<sup>33</sup> protocatechuic acid,<sup>34</sup> kojic acid (2-hydroxymethyl-5-hydroxy-8-pyrone),<sup>35</sup> ammonium sulfide,<sup>36</sup> ferrocyanide, and hydrochloric acid.<sup>37</sup>

<sup>22</sup> F. Alten, H. Weiland, and E. Hille, *Z. anorg. allgem. Chem.*, **215**, 81 (1933); A. Thiel and E. van Hengel, *Ber.*, **70**, 2491 (1937).

<sup>23</sup> J. P. Mehlig, *Ind. Eng. Chem., Anal. Ed.*, **10**, 136 (1938); R. O. Scott, *Analyst*, **66**, 142 (1941).

<sup>24</sup> D. E. Howe and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **12**, 448 (1940).

<sup>25</sup> J. H. Yoe, *J. Am. Chem. Soc.*, **54**, 4139 (1932); J. H. Yoe and R. T. Hall, *ibid.*, **59**, 872 (1937); H. W. Swank and H. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 406 (1937).

<sup>26</sup> See p. 97.

<sup>27</sup> A slightly soluble green-black ferric oxinate is formed above pH 3 which can be extracted with chloroform or filtered off and dissolved in alcohol (J. Lavollay, *Bull. soc. chim. biol.*, **17**, 432 (1935)). Vanadium reacts similarly.

<sup>28</sup> A. Combes, *Compt. rend.*, **105**, 868 (1887); H. Pulsifer, *J. Am. Chem. Soc.*, **26**, 967 (1904).

<sup>29</sup> A. L. Bernoulli, *Helv. Chim. Acta*, **9**, 835 (1926).

<sup>30</sup> H. W. van Urk, *Pharm. Weekblad*, **63**, 1121 (1926).

<sup>31</sup> G. Denigès, *Compt. rend.*, **180**, 519 (1925).



### III. Applications

#### A. GLASS SAND

##### ¶ Procedure<sup>38</sup>

Fuse 0.5 g. of sample with 5 g. of sodium carbonate. Treat the melt with dilute hydrochloric acid, evaporate to dryness, and remove silica in the usual way by double dehydration with hydrochloric acid. Combine the silica precipitates, ignite, and volatilize silica in the customary manner with hydrofluoric-sulfuric acid. Fuse the non-volatile residue with a gram of sodium carbonate, dissolve the melt in dilute hydrochloric acid, and add the solution to the filtrate from the silica. Add 1 ml. of concentrated nitric acid to the solution, boil for a minute or two, and add an excess of ammonia. Allow the precipitate to settle, filter, and wash with hot water. Dissolve the precipitate in 10 or 20 ml. of 1:1 hydrochloric acid and dilute the solution to 100 ml. in a volumetric flask. Determine iron in a 25 ml. aliquot by the thiocyanate or other method. Run a blank through the procedure.

#### B. WATER

Iron must often be concentrated in some fashion before it can be determined in natural waters. One way of doing this involves precipitation of ferric hydroxide with hydrous manganese dioxide as collector as described on p. 270. This method is not applicable to samples containing substances inhibiting the precipitation of iron hydroxide, and perhaps had best be avoided when the water is colored by organic substances. Another method, commonly used, calls for concentration of the iron by evaporation of the sample:

##### ¶ Procedure<sup>39</sup>

Evaporate 100 ml. of water to dryness in a silica or porcelain dish and if there is evidence of the presence of organic matter ignite the residue *gently*.<sup>40</sup>

<sup>32</sup> C. P. Sideris, *Ind. Eng. Chem., Anal. Ed.*, **14**, 756 (1942).

<sup>33</sup> See p. 261 (Paulais).

<sup>34</sup> R. S. Pereira, *J. Biol. Chem.*, **137**, 417 (1941).

<sup>35</sup> M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 612 (1941).

<sup>36</sup> L. Roelen, *Z. anal. Chem.*, **117**, 385 (1939). A bluish green colloidal dispersion of ferrous sulfide is formed in a basic tartrate medium; the method is useful for determining iron in aluminum.

<sup>37</sup> See p. 106 and also R. Havemann, *Angew. Chem.*, **54**, 263 (1941).

<sup>38</sup> G. E. F. Lundell and H. B. Knowles, *J. Am. Ceram. Soc.*, **11**, 122 (1928). Also see A. Thürmer, *Glashütte*, **68**, 857 (1938).

<sup>39</sup> The directions given are similar to those in *Standard Methods for the Examination of Water and Sewage*, American Public Health Association, 7th Ed., 1933; p. 48.

<sup>40</sup> If desired, the sample can be evaporated in Pyrex and any organic matter in the residue destroyed by heating with nitric and perchloric acids. This is a more certain method of getting all the iron in solution, if destruction of organic matter is required.

To the cool dish, add 1 ml. of 1:1 hydrochloric acid, followed by a milliliter or two of water, and heat for 10 minutes on the steam bath to bring all soluble material into solution. Dilute with 10 ml. of water,<sup>41</sup> add a drop of 0.1 *N* potassium permanganate, and determine iron by the thiocyanate method (p. 268). The *o*-phenanthroline and mercaptoacetic acid methods may also be used, in which case the addition of permanganate is omitted. These methods are to be preferred if the sulfate content of the water is very high.

### C. BIOLOGICAL MATERIALS

Destruction of organic matter by ignition has some attractive features: the blank can be kept low and a relatively small sample can be used since the volume of the final solution is easily kept small. On the other hand, all the iron present in the sample may not be recovered unless precautions are taken. There is a possibility of loss of iron by interaction of the ash with the material of the dish (silica or porcelain) if too high a temperature is used or the quantity of ash is very small, by volatilization if much chloride is present,<sup>42</sup> and as a result of retention by silica or other insoluble material remaining after treatment of the ash with acid. Pyrophosphate is formed on ignition and if much is present it must be converted to phosphate by heating the acid solution or allowing it to stand for some time, before iron can be determined satisfactorily. These difficulties are avoided in wet-oxidation with acids.

Directions are given below for both methods of decomposing the sample. The exact procedure will vary from one biological material to another, and these directions should be looked upon merely as a guide which may require greater or less modification for a particular sample. The *o*-phenanthroline (or  $\alpha,\alpha'$ -bipyridyl) method is recommended for the final determination of the iron; it is not subject to error by the presence of sulfate, phosphate (but somewhat by pyrophosphate), and the trace metals of biological materials occurring in the usual quantities.<sup>43</sup> Much copper should be precipitated with hydrogen sulfide in acid solution. If copper does not exceed 0.2 mg. in a final volume of 25 ml. it will not interfere appreciably.

<sup>41</sup> If there is any appreciable residue after dilution, filter it off, and examine it for iron after treatment with hydrofluoric-sulfuric acid in the usual manner.

<sup>42</sup> According to C. Hoffman, T. R. Schweitzer, and G. Dalby, *Ind. Eng. Chem., Anal. Ed.*, **12**, 454 (1940), such losses are prevented by treating the sample with sodium hydroxide solution before ignition.

<sup>43</sup> S. H. Jackson, *Ind. Eng. Chem., Anal. Ed.*, **10**, 302 (1938), encountered an interfering substance or substances, not identified, in certain food products, which led to low results in the  $\alpha,\alpha'$ -bipyridyl method, whether organic material was destroyed by ignition or wet-oxidation. He recommends separation of the iron by precipitation as sulfide in ammoniacal solution to avoid this error.

Those wishing further information on the determination of iron in materials of biological origin are referred to the recent papers mentioned below.<sup>44</sup>

### ¶ Procedure

**Ashing by Ignition.**—Take 3–4 g. of sample for iron contents in the neighborhood of 10 p.p.m. and ash at 550° C. in a silica or porcelain dish.<sup>45</sup> A muffle furnace, not a burner, should be used. Add 5 ml. of 1:2 hydrochloric acid and warm until it is judged that all soluble material has been brought into solution. Dilute with water and filter through a small paper (previously washed with hot dilute hydrochloric acid) into a 25 or 50 ml. volumetric flask. Wash with small portions of hot water. If there is a significant amount of insoluble material (carbon, silica, etc.), ignite the paper and its contents in a platinum crucible<sup>46</sup> until a light-colored residue is obtained. Add a drop or two of 1:1 sulfuric acid followed by 1–2 ml. of hydrofluoric acid and evaporate to fumes of sulfuric acid. Cool, rinse down the sides of the crucible with water, add 1–2 drops of sulfuric acid, and again evaporate to fumes. Add 1–2 ml. of water to the crucible, warm and rinse into the volumetric flask (filter the solution in the crucible if it is not quite clear after diluting with more water).

Dilute the solution in the volumetric flask to the mark and determine iron in a suitable aliquot (10/25 for 10–20 p.p.m. of iron in the sample) with *o*-phenanthroline (or  $\alpha,\alpha'$ -bipyridyl) according to the general directions on p. 273.<sup>47</sup> A blank must be run.

<sup>44</sup> (a) Thiocyanate method: R. Stugart, *Ind. Eng. Chem., Anal. Ed.*, **3**, 390 (1931); H. L. Roberts, C. L. Beardsley, and L. V. Taylor, *ibid.*, **12**, 365 (1940); C. Hoffman, T. R. Schweitzer and G. Dalby.<sup>42</sup> (b) Mercaptoacetate method: G. Leavell and N. R. Ellis, *Ind. Eng. Chem., Anal. Ed.*, **6**, 46 (1934); R. A. Koenig and C. R. Johnson, *J. Biol. Chem.*, **142**, 233 (1942). (c) *o*-Phenanthroline and  $\alpha,\alpha'$ -bipyridyl method: Jackson;<sup>43</sup> F. C. Hummel and H. H. Willard, *Ind. Eng. Chem., Anal. Ed.*, **10**, 14 (1938). L. G. Saywell and B. B. Cunningham, *Ind. Eng. Chem., Anal. Ed.*, **9**, 67 (1937). R. A. Koenig and C. R. Johnson, *J. Biol. Chem.*, **143**, 159 (1942); R. H. Thorp, *Biochem. J.*, **35**, 672 (1941); K. H. Schaefer, *Biochem. Z.*, **304**, 417 (1940).

<sup>45</sup> If there is a possibility of volatilization of iron (appreciable amounts of chloride present), 4–5 ml. of 1 *N* sodium hydroxide solution may be mixed with each gram of sample before drying and igniting. It is more difficult to burn off the carbon when sodium hydroxide is added, and it may be necessary to extract the black residue with dilute acid to remove the coating of salts, filter, wash with hot water, and then ash the paper and its contents.

<sup>46</sup> The crucible should be heated before use in 1:1 hydrochloric acid for several hours to remove iron.

<sup>47</sup> H. Cowling and E. J. Benne, *J. Assoc. Official Agr. Chem.*, **25**, 555 (1942), have shown that if much aluminum is present with phosphate in the sample, low results for iron are obtained by the Hummel-Willard procedure because iron is carried down in the aluminum phosphate precipitate then formed in the weakly acid solution. This interference is prevented by adding 2 ml. of 1 per cent ammonium citrate

**Wet Oxidation.**—Transfer 1–2 g. of sample (at least 20  $\gamma$  of iron should be present) to a small Kjeldahl flask,<sup>48</sup> moisten with water, and add 5 ml. of concentrated nitric acid and 2 ml. of concentrated sulfuric acid. Heat gently. When charring begins, add nitric acid in small portions (a few drops at the time)<sup>49</sup> and continue until on evaporation to fumes of sulfuric acid a colorless or very pale yellow liquid is obtained. Cool, add 2–3 ml. of water and evaporate to white fumes; cool, add another 2 ml. portion of water, and again evaporate to fumes.<sup>50</sup> Cool and dilute the solution to 25 ml. in a volumetric flask.<sup>51</sup>

Find the volume of 1:1 ammonia required to neutralize the acid in a 10 ml. aliquot of the diluted solution by adding a drop of methyl orange and titrating until the color just deviates from red. Transfer another 10 ml. aliquot to a 25 ml. volumetric flask, add the volume of ammonia found to be required for neutralization followed by 5 ml. of sodium acetate-acetic acid-hydroquinone solution (100 g. sodium acetate trihydrate, 400 ml. of glacial acetic acid, and 2 g. of hydroquinone diluted with water to 1 liter).<sup>52</sup> Add 1 ml. of 0.5 per cent *o*-phenanthroline solution and dilute to volume.<sup>47</sup> Determine the transmittancy after 1 hour. The standards for the construction of the reference curve should be treated in the same manner as the sample solution. A correction must be applied for the iron in the reagents.

before adjusting the pH to 3.5. Hydroxylamine cannot be used in place of hydroquinone for reduction of iron in the presence of citrate. It may also be mentioned that these authors found no interference from large amounts of pyrophosphate (50 mg. P: 0.1 mg. Fe) if the ash was digested at 100° for 15 minutes with 1:1 hydrochloric acid. Under these conditions, a 15 minute period of standing after the addition of *o*-phenanthroline usually is long enough for the full development of color.

<sup>48</sup> A 250 ml. Erlenmeyer flask may also be used. Place a small funnel in the mouth of the Erlenmeyer.

<sup>49</sup> If desired, the oxidation can be finished with perchloric acid. Add 1 ml. of the 60 per cent acid after the preliminary oxidation with nitric acid and heat at a slightly higher temperature than before until white fumes appear. If the solution is not colorless at this point continue the heating, adding more perchloric acid if necessary. Then continue as in the procedure above, adding water and evaporating to fumes to destroy any nitrosyl sulfuric acid that may be present.

<sup>50</sup> If calcium sulfate separates, destroy nitrosyl sulfuric acid by adding 1 ml. of 30 per cent hydrogen peroxide (or ammonium persulfate, p. 318) to the warm concentrated sulfuric acid.

<sup>51</sup> If the solution should contain any insoluble material, filter into the volumetric flask. The washed residue on the filter paper should preferably be examined for any iron it may contain (*cf.* p. 13).

<sup>52</sup> Dissolve the hydroquinone in the sodium acetate-acetic acid solution as needed, since the reagent becomes discolored and ineffective on standing.

## CHAPTER XXIV

### LEAD

#### I. Separations

Important methods for the separation and isolation of small amounts of lead include dithizone extraction, sulfide precipitation, electrolytic deposition of lead dioxide or lead, coprecipitation of lead sulfate with strontium or barium sulfate, and precipitation of lead chromate or phosphate. The nature of the sample decides which method must be used in any particular case; sometimes two methods must be used in conjunction with each other for satisfactory isolation.

##### 1. Dithizone Extraction

This frequently provides the simplest means of separating lead.

Lead can be completely extracted from a slightly basic solution, containing citrate or tartrate to prevent the precipitation of foreign metal hydroxides, by a small excess of dithizone in either carbon tetrachloride or chloroform. With the latter solvent the optimum  $pH$  range is 8.5–11,<sup>1</sup> and with the former it is approximately 8–10.<sup>2</sup> If a considerable excess of dithizone is used, as is generally the case in practical work, the extraction can be made quantitative at  $pH$  8 with chloroform as the solvent.<sup>3</sup>

In the presence of cyanide as complex-former the only other metals extracted are bismuth, thallium, and stannous tin. However, a number of substances may cause difficulties. Ferric iron in alkaline cyanide medium gives ferricyanide which oxidizes dithizone, and when it is present in more than small amounts the  $pH$  should be kept as low as is consistent with the complete extraction of the lead, or hydroxylamine hydrochloride should be added. Copper also tends to oxidize dithizone in basic medium. Large amounts of cyanide render the extraction of lead more difficult, and there is accordingly a limit to the quantity of foreign metals that may be present. The alkaline solution must be free from any precipitate that is likely to

<sup>1</sup> P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **19**, 134 (1936).

<sup>2</sup> H. Müller, *Z. anal. Chem.*, **113**, 164 (1938).

<sup>3</sup> The nature of the anion present has a considerable effect on the completeness of extraction at different  $pH$  values. Thus, L. P. Biefeld and T. M. Patrick, *Ind. Eng. Chem., Anal. Ed.*, **14**, 275 (1942), found that under otherwise constant conditions, lead was extracted by chloroform to the extent of 90 per cent at a  $pH$  of (a) 6.3 in hydrochloric acid-cyanide medium, (b) 6.8 in acetate solution, (c) 7.3 in tartrate-ammonia solution, (d) 8.5 in cyanide-citrate-ammonia solution. In ammoniacal citrate-cyanide medium a  $pH$  of 9.5 is required for virtually complete extraction.

occlude lead (*cf.* p. 92). The dithizone extraction fails in the presence of much calcium (or magnesium) and phosphorus. The phosphates of these metals are only slightly soluble in the ammoniacal citrate solution and carry down lead strongly. Stannic acid also carries down lead, and when much tin is present it must be removed, preferably by volatilization as the bromide (see p. 300).

Bismuth in small amounts ( $< 0.5$  or 1 mg.) has been separated from lead by extraction with dithizone in chloroform solution at pH 2.<sup>4</sup> The reaction is sluggish at this acidity. According to Fischer and Leopoldi,<sup>5</sup> bismuth should be extracted at pH 2.8 to 3.0 when a carbon tetrachloride solution of dithizone is used. According to these authors the extraction of bismuth is not quite complete at pH 3, but the amount remaining is too small to interfere in the subsequent colorimetric dithizone determination. At pH 3.6 to 4.0 lead may be slightly extracted. It is possible to determine lead with fair accuracy in the presence of as much as 5 mg. of bismuth by extracting all of the lead together with some of the bismuth from a solution containing a relatively high concentration of cyanide and then separating the co-extracted bismuth at pH 3 (see p. 290). Bambach and Burkey<sup>6</sup> separate lead and bismuth from each other by shaking the chloroform solution of the dithizonates with a buffer solution (phthalate) of pH 3.4. Lead goes into the aqueous phase and bismuth remains in the chloroform except when relatively much of it is present, in which case a little finds its way into the water layer, from which it can then be extracted with dithizone.

By fractional extraction from cyanide solution, lead can be separated tolerably well from thallium (see p. 291).

When determining lead in samples such as silicates and biological materials containing only minute amounts of heavy metals reacting with dithizone, it is frequently advantageous to isolate the lead by extracting the alkaline citrate solution (no cyanide present) with dithizone and then shaking the carbon tetrachloride (or chloroform) extract with dilute acid (0.02 *N* hydrochloric or nitric). Lead dithizonate is thus decomposed and ionic lead transferred to the aqueous phase, in which it is then readily determined. This procedure separates lead from copper (whose dithizonate is not appreciably decomposed by dilute acid) and iron, which are undesirable constituents of a solution in which lead is to be determined by the dithizone method, since they oxidize dithizone in basic medium as already mentioned.

<sup>4</sup> C. E. Willoughby, E. S. Wilkins, Jr., and E. O. Kraemer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 285 (1935). M. K. Horwit and G. R. Cowgill, *J. Biol. Chem.*, **119**, 553 (1937), extract bismuth at pH 3.0–3.5.

<sup>5</sup> H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **119**, 182, 184 (1940).

<sup>6</sup> K. Bambach and R. E. Burkey, *Ind. Eng. Chem., Anal. Ed.*, **14**, 904 (1942).

In many cases no special preliminary separation of lead from a cyanide solution is necessary; the metal is determined directly in the presence of others such as zinc after addition of cyanide by extraction with a standard dithizone solution.

### 2. Sulfide Precipitation

Minute quantities of lead can not be completely precipitated by hydrogen sulfide in dilute mineral acid solution, even if a collector such as copper or silver sulfide is used.<sup>7</sup> One must precipitate at a *pH* of about 3 in the presence of citrate to keep ferric and other phosphates in solution. A little copper is added to serve as a collector. Resort must be made to sulfide precipitation of lead in dealing with samples (bone-ash for example) containing much phosphate and calcium or magnesium, which are not amenable to dithizone extraction.

### 3. Electrolytic Deposition as Lead Metal or as Dioxide

Isolation of lead by electrodeposition as the metal from a solution of decomposed biological material has been recommended.<sup>8</sup> The lead is deposited on a rotating gauze cathode (5–6 volts, 0.2–0.5 ampere) from an ammoniacal citrate solution. Microgram quantities of lead can thus be recovered practically completely from 20–50 ml. of solution. The deposition of iron and copper is minimized by addition of potassium cyanide to the solution.

Electrodeposition of lead dioxide is frequently applied in the separation of small amounts of lead. For the conditions of electrolysis see p. 293. In the absence of considerable amounts of such substances as iron and phosphate it appears that satisfactory recoveries of lead can be obtained (see Table 42). Bambach and Cholak (*loc. cit.*) obtained poor recoveries of lead as dioxide from solutions containing iron or phosphorus when electrolyzing by the A.O.A.C. and other methods.

### 4. Coprecipitation with Strontium Sulfate

Mixed crystal formation between strontium and lead sulfates may be made the basis of a good method for the isolation of minute quantities of lead at high dilutions (p. 20). Rosenqvist (*loc. cit.*) found that practically complete recovery of lead could be obtained in this way. The precipitate of strontium-lead sulfate is fused with sodium carbonate and the melt leached with water to obtain strontium-lead carbonate which may be dissolved in acid after thorough washing to remove sulfate.

<sup>7</sup> I. T. Rosenqvist, *Am. J. Sci.*, **240**, 359 (1942).

<sup>8</sup> K. Bambach and J. Cholak, *Ind. Eng. Chem., Anal. Ed.*, **13**, 504 (1941).

### 5. Precipitation as Chromate or Phosphate

Lead chromate is but slightly soluble in weakly acid solutions (acetic acid-acetate) and is frequently used as an isolation form for small amounts of the metal. In nearly neutral solution (pH 6.6–7.4) a double chromate of lead and potassium is precipitated (see the reference on p. 94). Probably barium chromate can be used as a collector for lead chromate.

Minute amounts of lead can be successfully isolated by addition of ammonia to a solution containing calcium and phosphate.<sup>9</sup>

## II. Methods of Determination

### A. THE DITHIZONE METHOD

Dithizone is doubtless the best reagent for the determination of traces of lead. When properly carried out, the dithizone method gives excellent results,<sup>10</sup> but there are a number of sources of error that must be guarded against (p. 91).

The first procedures<sup>11</sup> described for the determination of lead were based on mono-color colorimetry, either of the red lead dithizonate or of the equivalent amount of dithizone obtained by shaking the solution of lead dithizonate in the organic solvent with a dilute acid. Such a method involves a source of error, because the excess of dithizone in the organic solvent must be removed by shaking with a weakly alkaline solution, and in this washing some lead may be lost as already pointed out (p. 84). Since the loss of lead increases with the alkalinity of the wash solution, the natural tendency is to use a solution very weakly basic, but then the extraction of dithizone becomes more difficult and some of it may be left in solution (the use of a suitable filter in the color comparison minimizes this error). Clifford and Wichmann<sup>12</sup> have given some figures on the extent of loss of lead dithizonate on washing. When 25 ml. of a carbon tetrachloride solution of lead dithizonate containing 35.8  $\gamma$  of lead were shaken with an equal volume of 1:200 ammonia for one minute, 6.4  $\gamma$  of lead were found in the aqueous phase. In an actual determination the loss would be smaller because less

<sup>9</sup> L. T. Fairhall and R. G. Keenan, *J. Am. Chem. Soc.*, **63**, 3076 (1941). According to these authors coprecipitation of lead with calcium oxalate is not satisfactory.

<sup>10</sup> For a comparison of the spectrographic, dithizone, and diphenylcarbazine methods for the determination of lead in biological material see J. Cholak, D. M. Hubbard, R. R. McNary, and R. V. Story, *Ind. Eng. Chem., Anal. Ed.*, **9**, 488 (1937). These authors conclude that the dithizone and spectrographic methods give equally good results, although the latter is preferable when only a limited amount of sample is available. Results by the diphenylcarbazine method are low (–0.07 mg.), but the method is useful when relatively large quantities of lead are involved.

<sup>11</sup> H. Fischer and G. Leopoldi, *Wiss. Veröffentlich. Siemens-Konzern*, **12**, 44 (1933); *Z. angew. Chem.*, **47**, 90 (1934).

<sup>12</sup> P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **19**, 140 (1936).



ammonia is used in washing, and excess dithizone is originally present. If chloroform is used as the solvent the loss in a single washing is smaller but this is counterbalanced by the larger number of extractions required to remove dithizone completely from this solvent. In order that good results may be obtained in the mono-color method, the standard solution must be prepared in the same manner as the unknown and must contain very nearly the same amount of lead.<sup>13</sup> The standard series method is preferable to the balancing method. The standard series technique when properly applied is of course not subject to the errors mentioned.

### 1. The Mixed-Color Method

In this method the lead must first be brought into a solution having a definite volume and acidity. This is readily done by extracting the sample solution with dithizone as many times as may be necessary to remove all of the lead, and then shaking the carbon tetrachloride or chloroform lead dithizonate solution with dilute acid to transfer lead to the aqueous phase. After bringing the solution to the proper pH (approximately 9.5) by adding an ammoniacal citrate (or tartrate) solution, together with cyanide, it is shaken with a suitable excess of a chloroform solution of dithizone.

The concentration of lead dithizonate in the organic solvent solution originally containing a fixed concentration of dithizone can evidently be found by (a) measuring the absorption of blue-green light by the lead dithizonate in the solution, or (b) measuring the absorption of red light by the excess dithizone in the liquid, and referring the results to a standard curve, which has been constructed under the same conditions.<sup>14</sup> Method (b) is inherently more sensitive, because lead dithizonate shows very little absorption above 600  $m\mu$ <sup>15</sup> (Fig. 18, p. 86), whereas dithizone absorbs appreciably at and near 520  $m\mu$ , the wave length at which lead dithizonate shows maximum absorption. The applicability of method (b) requires that most of the original dithizone remain in the organic solvent phase. This condition is satisfied when a chloroform solution of dithizone is used

<sup>13</sup> According to Clifford and Wichmann,<sup>12</sup> results accurate to about 1  $\gamma$  can be obtained by the mono-color method.

<sup>14</sup> There is a third possibility, which has been applied by F. L. Kozelka and E. F. Kluchesky, *Ind. Eng. Chem., Anal. Ed.*, **13**, 484 (1941), viz., the transmittancy of the dithizone-lead dithizonate solution is determined at two wave lengths (520 and ca. 660  $m\mu$ ) corresponding to regions of strong absorption by lead dithizonate and dithizone respectively. The lead concentration can then be found from a nomograph in which the concentration is referred to the logarithms of the transmittancies at the two wave lengths.

<sup>15</sup> This, and other wave lengths mentioned in this paragraph, applies specifically to a carbon tetrachloride solution, but the corresponding values for chloroform solution are much the same.

and the  $pH$  of the aqueous phase is 9.5–10, *i.e.* that at which most of the lead in the system is present as the dithizonate. In, and near, this region the partition of dithizone between the two phases is more sensitive to a slight change in  $pH$  than is the partition of lead dithizonate, so that if the possibility of a slight variation in  $pH$  exists, method (a) would be preferred. However, the  $pH$ , can usually be kept constant without difficulty.

Either method gives a linear relation between extinction and the concentration of lead dithizonate if sensibly monochromatic light is used in the measurements, since dithizone and lead dithizonate obey Beer's law in chloroform and carbon tetrachloride.

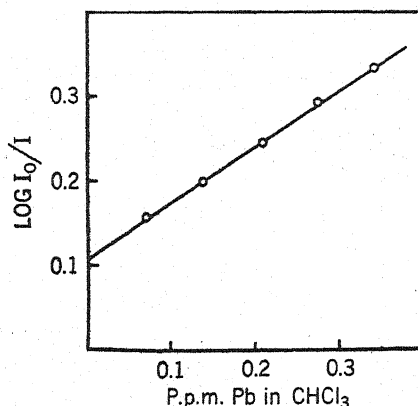


Fig. 39.—Determination of lead with dithizone by the mixed color method. 50 ml. of 1:100  $HNO_3$  solution of lead (10 to 50  $\gamma$ ) treated with 10 ml. of ammonia-cyanide mixture and shaken with 20 ml. of 0.001% dithizone in chloroform; 2 ml. of extract diluted to 14.7 ml. and transmittancy determined in a 1.3 cm. cell at *ca.* 510  $m\mu$  (water in reference cell). (Data of Arthur Anderson, Division of Industrial Hygiene, Minnesota State Board of Health.)

The following directions are particularly intended for the determination of traces of lead in biological material after suitable preparation of sample (p. 298), but they may be applied in many cases to other classes of material with but little modification. The procedure is similar to that described by a number of workers.<sup>16</sup>

<sup>16</sup> Especially K. Bambach, *Ind. Eng. Chem., Anal. Ed.*, **11**, 400 (1939); D. M. Hubbard, *ibid.*, **9**, 493 (1937); P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **19**, 130 (1936). For a procedure by which lead and bismuth can be co-determined by measurement of the transmittancy of the carbon tetrachloride solution of the dithizonates at *ca.* 450, 510, and 560  $m\mu$ , see P. A. Clifford, *J. Assoc. Official Agr. Chem.*, **26**, 26 (1943).

## Reagents

*Water.* Distilled from Pyrex. It should give no test for lead.

*Chloroform.* Redistilled (p. 90).

*Dithizone solution (A),* 50 mg. of dithizone (not specially purified) in 1 liter of chloroform. Protect from light.

*Dithizone solution (B),* 50 mg. of purified dithizone in 1 liter of redistilled chloroform. Keep in the dark, preferably in an ice box. One per cent alcohol may be added to make the solution more stable (p. 90).

*Ammonium hydroxide.* Pass ammonia from a cylinder into cold redistilled water until saturated, or if tank ammonia is not available, distil a concentrated solution.

*Nitric acid, 1:100.* Dilute colorless concentrated acid previously distilled from Pyrex if necessary,<sup>17</sup> with 100 times its volume of water.

*Ammonium citrate solution,* 50 g. in 100 ml. of water. Make the solution ammoniacal (pH 8.5-9) and shake with successive portions of dithizone (solution A) until all lead has been removed. Remove any excess dithizone by shaking with chloroform..

*Potassium cyanide solution,* 10 g. in 100 ml. of water. If necessary potassium cyanide can be freed from lead as follows. Prepare an approximately saturated solution (50 g. in 100 ml. of solution) and shake with successive small portions of dithizone until all lead has been removed (green color in final chloroform extract). Extract the dithizone in the aqueous layer with chloroform, and dilute to 10 per cent.

*Hydroxylamine hydrochloride solution,* 20 g. in 100 ml. of water. If necessary lead and other heavy metals may be removed in the following way. Add ammonium hydroxide to 20 g. of the reagent in about 65 ml. water containing a few drops of m-cresol purple until a yellow color appears and then add a milliliter of 5 per cent solution of sodium diethyldithiocarbamate. Extract the solution with chloroform until the metal carbamates and all of the excess reagent are removed. Complete extraction of reagent may be tested by shaking the chloroform extract with a dilute copper solution; no yellow color should appear. Then add hydrochloric acid (redistilled if necessary) to the hydroxylamine hydrochloride solution until the indicator turns pink, and dilute to 100 ml. with water.

*Ammonia-cyanide solution,* 20 g. of potassium cyanide and 150 ml. of concentrated (sp. gr. 0.90) ammonia diluted to 1 liter with distilled water.

*Standard lead solution,* 0.00100 per cent in 1:100 nitric acid. This solution is preferably prepared fresh before use by dilution of a 0.100 per cent solution (0.160 g. of dried lead nitrate in 100 ml. of solution acidified with nitric acid).

## ¶ Procedure

**Isolation of Lead.**—Transfer the sample solution, or a suitable aliquot of it, containing from 1 to 100  $\gamma$  of lead, to a glass-stoppered separatory funnel. Add 15 ml. of ammonium citrate and 1 ml. of hydroxylamine hydrochloride solution together with a few drops of thymol blue indicator. Next add ammonium hydroxide until the solution is basic, and then 5 ml. (or more if required) of potassium cyanide solution. Adjust the pH of the solution to 8.5-9 (greenish color of indicator), add 2 to 5 ml. of dithizone solution A, and shake for 15 seconds. If the amount of lead present is not known even

<sup>17</sup> Concentrated analytical-reagent acid may contain 10-30  $\gamma$  lead per liter.

approximately, it is usually advisable to add the dithizone in increments of, say, 1 ml. with shaking after each addition until the color begins to deviate from the pure red of lead dithizonate, in order that an idea of the amount present may be gained for use later in the final determination. One milliliter of pure 0.005 per cent dithizone is equivalent to about 20 micrograms of lead.

Draw off the chloroform into another separatory funnel, extract the sample solution with another portion of dithizone (2–5 ml.), add this extract to the first, and extract a third time if necessary. The last extract should show no mixed color. Shake the combined chloroform extracts with 10 to 20 ml. of water, draw off the chloroform into a separatory funnel, extract the aqueous solution with 1 or 2 ml. of dithizone, and add the latter to the main dithizone extract.

Shake the chloroform extract with two successive 25 ml. portions of 1:100 nitric acid. Virtually all of the lead will pass into the first portion of acid; the second portion serves mainly the purpose of rinsing out the funnel. If an aliquot of the solution is to be taken, transfer the aqueous extracts to a 50 ml. volumetric flask and make up to the mark; otherwise combine them in a separatory funnel. If the presence of bismuth is suspected, it may be tested for and removed at this point (see note 4). Remove any droplets of dithizone by shaking with a little chloroform and drawing off. Swirl the solution in the funnel to collect droplets of chloroform into one globule and draw this off, leaving the bore of the stopcock filled with chloroform. If there is a film or drop of chloroform on the surface of the aqueous solution, allow the funnel to stand unstoppered until it has evaporated. Dry the stem of the funnel with a roll of filter paper.

**Determination of Lead.**—The isolated lead may be determined in a number of ways:

(a) *By photometry at 510  $m\mu$*  (determination of absorption by lead dithizonate).—If an aliquot of the solution containing the isolated lead is taken, dilute to 50 ml. with 1:100 nitric acid. Depending on the approximate amount of lead, as estimated from the volume of dithizone required in the extraction above, add a suitable volume (accurately measured) of standard dithizone solution prepared by diluting solution B with pure chloroform<sup>18</sup>:

Range of lead $\gamma$	Dithizone concentration, mg. per liter	Volume of dithizone, ml.
0–5	5	5
0–10	10	5
0–25	10	10
0–50	10	20
0–100	10	35

<sup>18</sup> The cell length to be used in the subsequent photometry of the solution will depend upon the type of instrument, *i.e.*, whether a photoelectric or visual photometer,

Then add 10.0 ml. of ammonia-cyanide mixture, shake for 1 minute, and allow the phases to separate. If the chloroform is red—indicating that a sufficient excess of dithizone is not present—add another 5 ml. portion of 0.001 per cent dithizone solution and shake again. Run a small volume of the chloroform solution through the stem of the funnel to displace the chloroform in the bore of the stopcock, and deliver the remainder of the clear solution into an appropriate absorption cell, which can be covered to prevent evaporation. Determine the extinction of the solution at  $510\text{ m}\mu$  (a Wratten compound filter No. 45 and No. 5 may be used). Use water as the reference liquid. Obtain the standard curve for each lead range by taking appropriate amounts of lead in 50 ml. of 1:100 nitric acid, saturating with chloroform, and proceeding as in the case of the sample solution. The 0.005 per cent stock solution (B) of dithizone in pure chloroform should show little change in a period of a few weeks if kept in the dark at  $10^{\circ}\text{C}$ . However, the transmittancy of the dilute dithizone solutions prepared from it by dilution should always be determined when the determination is made to avoid error due to a possible change in concentration from that existing at the time the standard curve was constructed.

(b) *By photometry at  $610\text{ m}\mu$*  (determination of absorption by the excess dithizone).<sup>19</sup>—Add 10 ml. of ammonia-cyanide solution to the nitric acid solution of the isolated lead and then 15 ml. of dithizone-chloroform solution containing 4 or 5 mg. per liter if the lead content falls in the range 0–15  $\gamma$ , or 15 ml. of dithizone solution containing 12 mg. per liter if the lead range is 15–50  $\gamma$ . If it is definitely known that the lead content is less than 5  $\gamma$ , greater accuracy can be obtained by using 15 ml. of dithizone containing 2 mg. per liter. Shake thoroughly, fill a 1 cm. cell with the chloroform phase (free from water droplets), and obtain the transmittancy of the solution at  $610\text{ m}\mu$ . By reference to a calibration curve find the lead content. It is advisable to check the calibration curve at the time the unknown solution is read. For the 0–15  $\gamma$  lead curve use a blank dithizone solution (15 ml., 4 mg. per liter) for checking, and for the 15–50  $\gamma$  curve use a 15  $\gamma$  lead standard. If the reading deviates from the corresponding point on the original calibration curve, the abscissas of the points on the curve may be displaced an equal distance, because the useful portions of all the curves are substantially parallel.

(c) *By the standard series method.*—Transfer an aliquot containing 0.5 to 3  $\gamma$  of lead to a  $1.8 \times 15\text{ cm.}$  glass-stoppered tube, add 1.0 ml. of ammonia-cyanide solution for each 5 ml. of lead solution (in 1:100 nitric acid) and 2.0 ml. of dithizone solution containing 8 or 10 mg. per liter of chloroform.

and of course, upon the filter, if one is used. If the solution is too strongly colored for satisfactory transmittancy measurement it should be diluted to a definite volume with pure chloroform.

<sup>19</sup> C. L. Guettel, *Ind. Eng. Chem., Anal. Ed.*, **11**, 639 (1939).

Shake vigorously for 10 or 15 seconds, allow the chloroform to settle and compare its hue with that of the chloroform layers in an appropriate series of standards obtained in the same manner. View the tubes against a white background.

For less than 0.5  $\gamma$  of lead use 1 ml. of dithizone solution.

(d) *By colorimetric titration.*—Transfer an aliquot containing up to 5  $\gamma$  of lead to a glass-stoppered tube ( $1.8 \times 15$  cm.). For efficient shaking the volume of the solution should not exceed 10 ml. Add 1.0 ml. of ammonia-cyanide solution for each 5 ml. of solution, and then with shaking after each addition, sufficient dithizone solution (8–10 mg. per liter of chloroform) to give a suitable mixed color (blue-violet to red-violet) for comparison. To a second similar tube add the same volumes of 1:100 nitric acid, ammonia-cyanide, and dithizone as present in the first tube. Now, from a buret or pipet graduated to 0.01 ml. add 0.001 per cent lead solution to the comparison tube, shaking well after each addition, until the hue of the chloroform layer matches that of the chloroform in the tube containing the sample solution.

**Notes.**—1. The amount of lead found must be corrected for lead introduced in the reagents or from the apparatus by running a blank through all the steps of the procedure, including the preparation of the sample.

2. The final solution of lead dithizonate should not be exposed to strong light. It may be kept for 12 hours and probably longer without appreciable change if stored in an ice box and protected from evaporation. However, the best policy is to determine the transmittancy of the solution as soon as it has been obtained, especially if very small amounts of lead are involved.

3. Phosphate is an undesirable impurity in potassium cyanide since it may precipitate lead in the final solution and cause low results, especially if the solution is allowed to stand for some time before extraction with dithizone. Therefore, as soon as the ammonia-cyanide solution has been added to the sample solution the latter should be shaken with dithizone. Potassium cyanide may be purified by preparing a hot saturated solution and boiling down but usually such purification is not necessary.

4. To separate bismuth from lead proceed as follows. Add 2 drops of thymol blue indicator to the solution (p. 286, line 19), and adjust the pH to 3.0 or a slightly greater value by carefully adding dilute ammonia until the indicator shows its full yellow color (add thymol blue to an equal volume of water for comparison). Shake the solution with 1–2 ml. of 0.001 per cent (weight/volume) dithizone for 2 minutes. If the chloroform remains green no appreciable amount of bismuth is present. An orange or mixed color shows bismuth, which then must be removed by shaking with successive small portions (2–3 ml.) of 0.005 per cent dithizone until the last portion remains an unchanged green after shaking for 2 or 3 minutes. Finally, to be certain that bismuth has been completely extracted, test the aqueous solution by shaking with 1–2 ml. of 0.001 per cent dithizone for at least 2 minutes. The chloroform should remain an unchanged green. Then adjust the pH of the solution to 8.5 with ammonia, and continue the determination according to the above directions.

The procedure of Bambach and Burkey (p. 280) may also be followed in separating lead from bismuth.

5. When tin is present, special treatment of the sample is necessary (see p. 300 and p. 456).

## 2. The Mono-Color Method<sup>20</sup>

As already stated this method is less accurate than the mixed-color method, but it lends itself better to the determination of lead in the presence of much bismuth and especially of much thallium.

TABLE 40  
DETERMINATION OF LEAD BY THE DITHIZONE MIXED-COLOR METHOD  
(CHLOROFORM, 510 M $\mu$ )

Lead taken, $\gamma$ .....	2.0	5.0	10.0	20.0	30.0	40.0	50.0
Lead found, $\gamma$ .....	2.0	5.0	11	20	30	41	49.5

### Reagents

*Dithizone solution*, 6 mg. of purified dithizone in 100 ml. of redistilled carbon tetrachloride.

*Ammonium hydroxide*. See p. 285.

*Hydroxylamine hydrochloride solution*, saturated solution of analytical reagent in cold water. Prepare shortly before use.

*Potassium cyanide solution (A)*, 5 or 10 per cent, lead-free.

*Potassium cyanide solution (B)*, 0.5 per cent, lead-free.

*Ammonium citrate solution*, 50 g. in 100 ml. of water. Remove lead from the solution by extracting with dithizone solution. See p. 285.

*Standard lead solution*. See p. 285.

### Procedure

If metals precipitated by ammonia are present, treat the solution with a sufficient amount of ammonium citrate to prevent their precipitation, and add enough ammonia to make the solution basic to litmus paper. Add enough potassium cyanide solution (A) to convert foreign heavy metals into their cyanide complexes. In the usual case 3 to 5 ml. of 5 per cent potassium cyanide per 10 ml. of sample solution will suffice, but when traces of lead are to be determined in the presence of much zinc, copper, silver, etc., 10 ml. or more of 10 per cent potassium cyanide may be needed. To prevent the interference of oxidizing substances such as ferric iron, add a milliliter of hydroxylamine hydrochloride solution, heat the solution to boiling, and cool to room temperature. Extract the solution in a separatory funnel with small portions (3–5 ml.) of dithizone until the carbon

<sup>20</sup> H. Fischer and G. Leopoldi, *Z. anal. Chem.*, 119, 164 (1940).

tetrachloride layer shows no red color. Shake the combined extracts, separated from the aqueous phase, with a few milliliters of potassium cyanide solution (B), and draw off the carbon tetrachloride layer. Again wash the latter with potassium cyanide solution. After the second washing the carbon tetrachloride phase should be virtually free from dithizone and the aqueous phase should be practically, if not entirely, colorless. Finally wash with a few milliliters of water.

The final determination of the lead can naturally be made in a number of ways. After the lead dithizonate solution has been made up to a definite volume with carbon tetrachloride, its transmittancy can be obtained with a spectrophotometer or a filter photometer (a filter giving maximum transmission at 520–530  $m\mu$  is suitable), and the lead concentration obtained from a calibration curve. Comparison may be made against a standard lead dithizonate solution with the aid of a Duboscq colorimeter, or the standard series method may be applied (*cf.* the determination of lead in silicate rocks, p. 296).

It may be advantageous to convert lead dithizonate into the equivalent amount of dithizone by shaking the carbon tetrachloride solution with 0.1–0.2 *N* nitric acid, and to measure or compare the color intensity of the resulting green solution (use a filter giving maximum transmission at 610  $m\mu$ ). To remove water droplets from the carbon tetrachloride it is permissible to filter the latter through a small ashless filter paper which has been washed with dilute nitric acid and then dried at 100°. The dithizone solution for comparison must be obtained from a known amount of lead which has been treated in exactly the same manner as the sample.

**Determination of Lead in the Presence of Much Bismuth (1 mg.).**—The sample solution should contain not more than 25  $\gamma$  of lead nor more than 5 mg. of bismuth. Add 1 ml. of ammonium citrate solution and then ammonia until slightly basic (litmus paper). For each 10 ml. of solution add 10 ml. of 10 per cent potassium cyanide solution, and shake 3 to 5 minutes with 2 ml. of dithizone solution containing 3 mg. of dithizone in 100 ml. of carbon tetrachloride. A mechanical shaker is convenient; the extraction of lead is slow in the presence of much bismuth. Separate the carbon tetrachloride, extract with another 2 ml. portion of dithizone, and continue in this way until the color of the last extract is pure orange (bismuth dithizonate). To be certain that all of the lead has been extracted, shake the last portion of carbon tetrachloride extract with three small portions of 1 per cent potassium cyanide solution. The carbon tetrachloride layer should show no pink color. If it does, extract the sample solution with another portion of dithizone. Shake the combined extracts, containing all of the lead and some bismuth, with 5 ml. of 1:100 nitric acid, separate the aque-



ous phase, adjust its pH to 2.8–3 (full yellow color of thymol blue) and shake with small portions of dithizone (6 mg. per 100 ml.) for 3–4 minutes until the dithizone remains pure green. Wash the aqueous solution with carbon tetrachloride, and determine lead according to the directions given above, after making the solution ammoniacal and adding 5 ml. of 5 per cent potassium cyanide and 1 ml. of hydroxylamine hydrochloride solution.

**Determination of Lead in the Presence of Thallium.**—To the sample solution containing up to 500  $\gamma$  of thallium add 0.5–1 ml. of ammonium citrate, make slightly ammoniacal, and add 10 ml. of 10 per cent potassium cyanide. Extract with about 2 ml. portions of dithizone solution containing 4 mg. dithizone in 100 ml. of carbon tetrachloride. The first extracts contain lead, and the latter ones lead with thallium or thallium alone. Both lead and thallium form red dithizonates and cannot be distinguished by inspection, but can be differentiated as follows. Shake each extract with twice its volume of 0.5 per cent potassium cyanide. Thallium dithizonate but not lead dithizonate is decomposed and the carbon tetrachloride is decolorized if the color is due to thallium alone.

Wash the combined carbon tetrachloride extracts with 0.5 per cent potassium cyanide solution to remove any excess dithizone, dilute to a definite volume with carbon tetrachloride and determine lead by the mono-color method.

**Notes.**—1. A 0.5 per cent potassium cyanide solution is preferable to 1:200 ammonia as wash solution, because the use of the latter may result in the reaction of heavy metals in droplets of aqueous solution in the drawn-off carbon tetrachloride phase.

The pH of 0.5 per cent potassium cyanide solution is about 11.4 and therefore some loss of lead may be expected when a carbon tetrachloride solution of lead dithizonate is washed with cyanide. Fischer and Leopoldi found that 19.6  $\gamma$  of lead extracted according to the above procedure and the carbon tetrachloride solution washed twice with 5 ml. of 0.5 per cent potassium cyanide (5 seconds shaking) and twice with 5 ml. of water gave an average recovery of 18.5  $\gamma$ . The error is reduced by compensation when the standard lead solution is treated similarly.

2. Conversion of lead dithizonate to dithizone may in some cases be advantageous because of the possibility of keeping dithizone solutions unchanged for a long time. A dithizone solution in carbon tetrachloride undergoes practically no change in a month if covered with a weakly acid solution of hydroxylamine hydrochloride and kept in a brown bottle in diffuse daylight (Fischer and Leopoldi). Tenth-normal sulfuric acid is nearly as effective as hydroxylamine hydrochloride in stabilizing dithizone solutions. On the other hand a lead dithizonate solution cannot be preserved unchanged for such a long period of time. If kept in a brown bottle a lead dithizonate solution shows practically no change in 4 days, but decomposes to a considerable extent in 15 days. Covering such a solution with a weakly alkaline cyanide solution increases the rate of decomposition (Fischer and Leopoldi).

3. When metals such as zinc, cadmium, etc. are present the excess of cyanide must be increased. In spite of the high alkalinity of the resulting solution, lead can be

extracted quantitatively if excess dithizone is used. In determining percentages of lead of the order of 0.001 in metallic zinc, 40 ml. of 10 per cent potassium cyanide are added to 5 ml. of solution containing 1 g. of zinc.<sup>21</sup>

TABLE 41  
DETERMINATION OF LEAD IN THE PRESENCE OF BISMUTH AND THALLIUM  
BY DITHIZONE<sup>22</sup>

Foreign metal	Pb taken $\gamma$	Pb found $\gamma$	Error $\gamma$
0.1 mg. Bi <sup>a</sup>	9.5	10.0	+0.5
0.1 mg. Bi <sup>a</sup>	9.5	9.0	-0.5
0.5 mg. Bi <sup>a</sup>	18.7	17.7	-1.0
1.0 mg. Bi <sup>a</sup>	7.4	7.1	-0.3
1.0 mg. Bi <sup>a</sup>	7.4	8.3	+0.9
5.0 mg. Bi <sup>b</sup>	9.8	8.3	-1.5
5.0 mg. Bi <sup>b</sup>	7.4	6.9	-0.5
0.15 mg. Tl	9.5	10.6	+1.1
0.3 mg. Tl	4.8	4.2	-0.6
0.75 mg. Tl	9.5	8.2-10.6	-1.3 to +1.1

<sup>a</sup> Bismuth extracted with dithizone at pH 2.8-3.0.

<sup>b</sup> Fractional extraction of lead from cyanide medium followed by removal of coextracted bismuth at pH 2.8-3.0 (see p. 290).

## B. THE TETRAMETHYLDIAMINODIPHENYLMETHANE METHOD

Lead can be determined colorimetrically by electrolytic deposition as dioxide followed by oxidation of tetramethyldiaminodiphenylmethane by the latter to an intensely colored blue diphenylmethane dye.<sup>23</sup>

The following procedure is that of Müller<sup>24</sup> who prefers this method to the dithizone method, especially when foreign metals such as iron, zinc, bismuth, and thallium are present. It may be used for amounts of lead above 5  $\gamma$ . Chloride and phosphate interfere seriously with the deposition of lead dioxide, and therefore lead must generally first be isolated as the sulfide.

### Reagent

*Tetramethyldiaminodiphenylmethane solution*, 50 mg. in 100 ml. of pure (redistilled) glacial acetic acid. The tetramethyldiaminodiphenylmethane should be recrystallized from hot alcohol containing a few drops of yellow ammonium sulfide, and the purified solid protected from light. The solution is stable for 24 hours.

<sup>21</sup> H. Fischer, *Metall u. Erz*, **35**, 87 (1938).

<sup>22</sup> Representative values from H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **119**, 183, 185 (1940).

<sup>23</sup> M. A. Trillat, *Compt. rend.*, **136**, 1205 (1903).

<sup>24</sup> H. Müller, *Z. anal. Chem.*, **113**, 161 (1938).

### ¶ Procedure

The solution of the isolated lead should have a volume not greater than 40 ml. and should contain about 12 mg. of copper and 4 to 6 g. of ammonium nitrate. Add ammonium hydroxide until the blue color of the copper ammonio complex just appears (it should be dischargeable by 1 drop of 20 per cent nitric acid) and then 0.5 ml. of 1 *N* nitric acid. Transfer the solution to the electrolysis vessel, dilute to 100 ml. or sufficiently to cover the electrodes. Use a gauze cylinder as anode and a rotating cathode (500–700 r. p. m.), Bring the temperature of the solution to 30–33° and electrolyze for 20 minutes with *ca.* 0.5 ampere and 2.3 volts. When deposition is

TABLE 42

DETERMINATION OF LEAD WITH TETRAMETHYLDIAMINODIPHENYLMETHANE AFTER ELECTROLYTIC DEPOSITION AS DIOXIDE<sup>25</sup>

Foreign elements $\gamma$	Pb taken $\gamma$	Pb found $\gamma$
	6	7.5
	8	9
	15	15
	17	18.5
	43	42
	63	60
100 Bi	0	1
500 Bi	0	0
50 Bi	15	20
500 Bi	20	18
2000 Zn	12	14
100 Tl	23	24
100 Mn	18	16.5
10000 Fe	10	14
10000 Fe	55	56
5000 Fe	6	8

complete, wash the electrodes thoroughly with water. Dip the anode in boiling water for 1 second, shake off droplets of water and immerse for one minute in a suitably sized vessel of annular cross section containing 25.0 ml. of freshly prepared tetramethyldiaminodiphenylmethane solution. Compare at once with a standard solution similarly obtained. Use a filter giving maximum transmission at 570  $m\mu$  or better at 600  $m\mu$  for amounts of lead less than 20  $\gamma$ .

**Notes.**—1. According to Müller not more than 1–2  $\gamma$  of lead will remain in solution after the electrolysis.

<sup>25</sup> H. Müller, *Z. anal. Chem.*, **113**, 161 (1938).

2. Although the author claims that good results can be obtained in the presence of foreign metals, especially bismuth, the figures given (*cf.* Table 42) are sometimes erratic. In pure solutions the accuracy is usually within 10 per cent for amounts greater than 8–10  $\gamma$ . It may be concluded that the method is inferior to the dithizone method properly carried out, especially below 5  $\gamma$ , when indeed the electrolytic method fails nearly altogether.

### III. Applications of the Dithizone Method

#### A. SILICATE ROCKS

The following procedure has been shown to give reliable results in the determination of lead in silicate rocks and minerals. The original directions,<sup>26</sup> worked out for the determination of lead by the mono-color standard series method with a carbon tetrachloride solution of dithizone have been retained, but it will be understood that after lead has been isolated it can be determined by other procedures if preferred, *e.g.*, according to the general method given on p. 286 with a chloroform solution of dithizone.

#### Special Reagents

*Dithizone*, 0.01 per cent (weight/volume) in carbon tetrachloride. Special purification of the solid dithizone is not necessary if the amount of the diazone (p. 88) present is small.

*Dithizone*, 0.001 per cent in carbon tetrachloride. Prepare by dilution of the 0.01 per cent solution shortly before use. The diluted solution shaken with a little dilute ammonia solution containing about 0.5 per cent potassium cyanide should give a practically colorless carbon tetrachloride layer.

*Perchloric acid*, 70 per cent. Redistillation is not necessary if a good grade of acid is used, unless lead contents of some parts per million are to be determined.

*Hydrofluoric acid*. This is likely to contain comparatively large amounts (1 or 2 p.p.m.) of lead and should be purified either by distillation from platinum or by coprecipitation of the lead with strontium fluoride (Rosenqvist, p. 281). In the latter case, add two 10 ml. portions of 10 per cent strontium chloride solution to 1 liter of concentrated hydrofluoric acid and decant off the supernatant liquid after standing. Care must be taken to see that there are no suspended particles of strontium fluoride in the liquid. In this way the lead content of the acid can be reduced to less than 0.002 p.p.m.

*Hydrochloric acid*, 1:1. Preferably redistilled.

*Hydrochloric acid*, 1:500 (*ca.* 0.02 *N*).

*Sodium or ammonium citrate*, 10 per cent. Make the solution weakly ammoniacal (1:200) and remove lead and other reacting metals by extracting with successive portions of 0.01 per cent dithizone until the carbon tetrachloride phase is colorless or at most shows a pink tinge.

*Potassium cyanide*, 5 per cent. A milliliter of solution should impart no pink color to the carbon tetrachloride phase when diluted with 2 ml. of water and shaken with a milliliter or two of 0.001 per cent dithizone.

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<sup>26</sup> E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, 9, 464 (1937). For typical results see Table 43.

*Sodium carbonate.* If necessary, the salt can be freed from lead by adding 1-2 ml. of 10 per cent strontium chloride dropwise to 100 ml. of nearly saturated solution, filtering off the precipitate, evaporating the filtrate in platinum, and gently igniting the residue.

### ¶ Procedure

**Decomposition of Sample.**—Weigh 0.25 g.<sup>27</sup> of 100-mesh rock powder into a platinum dish, and add a milliliter or two of water, 0.5 ml. of perchloric acid, and 3 ml. of concentrated hydrofluoric acid. Evaporate to dryness, occasionally stirring with a platinum spatula or wire to prevent caking, and expel the excess of perchloric acid. Add a few milliliters of water and 0.5 ml. of perchloric acid, again evaporate to dryness, and expel the excess of perchloric acid. To the residue add 2 ml. of 1:1 hydrochloric acid and 5 ml. of water, and warm if necessary to bring all soluble material into solution. Next add 5 ml. of ammonium or sodium citrate solution, cool to room temperature, and add ammonium hydroxide until the solution becomes basic to litmus paper and finally an excess of 0.25-0.3 ml. If the solution becomes turbid on the addition of ammonia allow it to stand for 15 minutes, and filter through a small paper (4-5 cm. in diameter) of medium texture, transfer any residue in the dish to the paper and wash with three or four 1 ml. portions of water containing a drop of ammonia and citrate solution. Reserve the filtrate (solution 1).

Ignite the paper and its contents in a platinum crucible, avoiding an unnecessarily high temperature. Mix the residue with 0.1-0.2 g. of sodium carbonate, fuse, and add a few milliliters of water to the melt. Warm to hasten disintegration, and filter the solution through a 4 cm. paper, keeping most of the residue in the crucible. Wash with small portions of water totaling 10 ml. Reserve the filtrate (solution 2), transfer the filter paper to the platinum crucible, and ignite at a low temperature. Add 1 ml. of hydrofluoric acid and 2-3 drops of perchloric acid, evaporate to dryness, and expel the perchloric acid; treat the residue with a few drops of water and 1-2 drops of perchloric acid, and again expel the excess acid. Add 1 ml. 1:1 hydrochloric acid and 2-3 ml. of water and warm to bring the residue into solution. (Any insoluble material should be re-fused with sodium carbonate.) Add 1 ml. of citrate solution and then ammonia in a 3 or 4-drop excess over that required for neutralization (solution 3).

**Isolation of Lead and Other Metals Reacting with Dithizone.**—Transfer the main solution (solution 1) to a small separatory funnel, add 5 ml. of

<sup>27</sup> If it is desired to use a photometer in the final determination it may be necessary to take a 0.5-0.75 g. sample in order that the volume of the carbon tetrachloride solution whose transmittancy is determined will be sufficiently large (5 ml.) to fill the cell used. If a larger sample is taken, increase the volume of the reagents proportionately.

0.01 per cent dithizone solution and shake for one-half minute.<sup>28</sup> If the dithizone is green shake for another half-minute. Allow the phases to separate and draw off the carbon tetrachloride into another separatory funnel. Unless the separated carbon tetrachloride is distinctly green, add another 5 ml. portion of dithizone, shake for one-half to one minute, draw it off, and continue in this manner until the last portion remains green after shaking for at least one-half minute. Next extract the solution of the leached sodium carbonate melt (solution 3) in the same way, except use 1-2 ml. portions of dithizone. Combine these extracts with the others. Finally, extract the filtrate from the sodium carbonate leach (solution 2) with 2 ml. of dithizone, after adding 0.5 ml. of citrate solution and sufficient dilute hydrochloric acid to give the greenish intermediate color of thymol blue.

Wash the combined carbon tetrachloride extracts with 2-3 ml. of water, separate the phases, shake the wash water with a milliliter of dithizone and add this to the washed carbon tetrachloride phase. It is important that the separated carbon tetrachloride be free from droplets of iron-containing solution.

**Separation of Lead (and Zinc) from Copper.**—Shake the combined carbon tetrachloride extracts for 1 minute with 10 ml. of 1:500 hydrochloric acid. If the carbon tetrachloride remains red on shaking add 1-2 ml. of 0.01 per cent dithizone before finishing the shaking. Draw off the carbon tetrachloride into another separatory funnel and shake vigorously for 1 minute with a fresh 10 ml. portion of 1:500 acid. Combine the two acid extracts, add a few drops of carbon tetrachloride and draw off to remove any colored droplets of carbon tetrachloride, transfer to a 25 ml. volumetric flask, and make up to the mark with the dilute acid. This solution contains the lead and zinc of the sample. The carbon tetrachloride contains the copper (see p. 228 for its determination).

**Determination of Lead.**—If the lead is to be determined by the standard series method, transfer 5 ml. of the solution to a color-comparison tube (p. 42), add 0.1 ml. each of citrate solution and concentrated ammonium hydroxide, and 1.0 ml. of potassium cyanide. Prepare a series of standards (containing for example 0, 0.5, 0.75 . . . 2  $\gamma$  of lead) in 5 ml. of the dilute acid and treat with citrate, ammonia, and cyanide. Without delay add 2.0 ml. of 0.001 per cent dithizone solution from a buret to unknown and standards. Shake the tubes well for 10-15 seconds and examine trans-

<sup>28</sup> If copper and zinc are not to be determined simultaneously, add also 1 ml. of potassium cyanide and 1 ml. of 20 per cent hydroxylamine hydrochloride to form cyanide complexes of these metals and prevent their extraction, thus reducing the volume of dithizone required. Add more ammonia if necessary to make the solution basic and proceed as above.

versely against a white background. If desired, adjacent members of the standard series may be mixed for a more precise comparison after the first comparison has been made.

If a photometer is used, take 5 or 10 ml. of the lead solution and add citrate, ammonia, and cyanide as specified in the preceding paragraph, except use 2 ml. of potassium cyanide for 10 ml. of lead solution. Shake with 2.0–3.0 ml. of 0.001 per cent dithizone. Determine the transmittancy of the carbon tetrachloride at 525  $m\mu$ , and refer the reading to a standard curve obtained under the same conditions.

A blank must be run to find the amount of lead contributed by the reagents.

TABLE 43  
DETERMINATION OF LEAD IN SILICATE ROCKS

Sample	Pb present %	Pb found %
Granite.....	0.0004	0.00025
Diabase.....	0.0008	0.0007
Granite.....	0.0008	0.0008
Granite.....	0.0035	0.0035
Gabbro.....	0.0047	0.0041
Granite.....	0.0055	0.0057
Granite <sup>a</sup> .....	0.0055	0.0051
Granite <sup>b</sup> .....	0.0015	0.0012

<sup>a</sup> Contained 0.4% Cr (III), 0.6% Ba, 0.25% S. Nitric acid used in place of perchloric acid in the decomposition.

<sup>b</sup> Contained 0.01% Ti, 0.02% Ag, 1% Sn.

## B. WATER

The amount of sample to be taken will depend on the magnitude of the lead concentration and the method of making the final color measurement or comparison. Precautions must be taken to prevent loss of lead by adsorption or by coprecipitation with any insoluble matter formed on standing. The sample should be acidified with hydrochloric acid immediately after collection.

If, as is generally the case, large amounts of metals reacting with dithizone are not present, the following procedure is suitable. Treat the sample with enough lead-free sodium or ammonium citrate to make its concentration about 2 per cent, make slightly ammoniacal ( $pH$  ca. 9), extract the lead and other reacting metals with successive portions of 0.01 per cent dithizone in carbon tetrachloride, and continue as described on p. 296 *et seq.* Should relatively much zinc or copper be present the general procedure given on p. 285 can be applied.

## C. BIOLOGICAL MATERIALS

Samples of organic origin may be decomposed by ashing or by digestion with oxidizing acids. The former method is more convenient in some respects but involves possible loss of lead by volatilization (?) and from retention by the surface of the dish, especially if the amount of ash is scanty. The acid digestion method is free from these sources of error, but is open to the objection that the blank may be unpleasantly large unless redistilled acids are used. Directions for both methods of decomposition follow.

## 1. Ashing

## ¶ Procedure

The amount of sample taken should in general be such that the aliquot of the final solution used for the colorimetric determination will contain 5–10  $\gamma$  of lead. Transfer the weighed sample to a porcelain casserole of suitable size having an unetched smooth glazed interior.<sup>29</sup> If the material is wet, dry it on the steam bath or a low temperature hot plate. If the sample is difficult to ash, or is very low in ash, add a few milliliters of aluminum nitrate-calcium nitrate solution,<sup>30</sup> mix, and dry. Now char the sample by heating carefully with a burner or on a hot plate giving a sufficiently high temperature. Then transfer the casserole to a muffle furnace equipped with a pyrometer and gradually raise the temperature to 500° C. The dish should be placed on an asbestos board or a clay triangle. The sample must not ignite. Continue the heating at 500° (not higher) until the carbon has disappeared. If the material is still dark after some hours, 2–3 ml. of aluminum-calcium nitrate solution may be added and the dried residue reheated for an hour. If the residue is still dark, 1–2 ml. of concentrated nitric acid may be added, the mixture dried, and cautiously heated.

Add 10 ml. (or more or less as deemed desirable) of hydrochloric acid and heat near the boiling point. If a clear solution is not obtained after heating for 30 minutes, evaporate to dryness on the steam bath and heat the residue for 15 minutes at 100–115° to dehydrate silica. Add 2–5 ml. of hydrochloric acid to the dish, followed by 5 ml. of water. Heat on the steam bath until all soluble material has been brought into solution, then add 3 to 5 ml. of ammonium citrate solution (p. 285) and heat for 10 minutes. If the amount of insoluble material (silica) is very small, filter the solution through a sintered glass or porous porcelain filter crucible and wash with a little dilute hydrochloric acid. If the amount of silica is appre-

<sup>29</sup> It is advisable to clean the dish before use by heating for a few minutes with 1 N sodium hydroxide solution and then rinsing with dilute nitric acid and water.

<sup>30</sup> 40 g.  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  and 20 g.  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$  in 100 ml. of water (*Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists*, 5th ed., p. 396).



ciable, filter the solution through a small ashless paper previously washed with dilute hydrochloric acid and wash the precipitate on the paper with dilute acid. Transfer the paper to a platinum crucible,<sup>31</sup> ignite, add a milliliter or so of hydrofluoric acid and a few drops of perchloric acid, and evaporate to fumes. Take up the residue in a few milliliters of dilute hydrochloric acid and add the solution to the main portion.

Make the cold acid-citrate solution ammoniacal (litmus paper as indicator) and allow it to stand for about 5 minutes. If no precipitate forms, proceed with the determination of lead as described on p. 285. If a precipitate forms (usually calcium or magnesium phosphate) add enough hydrochloric acid to the cold solution to dissolve it, and adjust the pH of the solution to 3-3.5. Add 5 mg. of copper sulfate, pass hydrogen sulfide into the solution for 5-10 minutes, and allow to stand for an hour or longer. Filter, preferably through a sintered glass or porous porcelain filter crucible; do not wash the precipitate. Dissolve the sulfides in a few milliliters of hot nitric acid, wash with water, and boil the solution to expel all hydrogen sulfide. Proceed with the determination of lead according to the directions on p. 285.

Make a note of the volume of all the reagent solutions used in order that the same quantities may be taken in the blank.

## 2. Acid Digestion

Sulfuric acid is best avoided in the digestion mixture, because, unless redistilled, it may introduce relatively large amounts of lead into the sample, and also it may form slightly soluble calcium sulfate which will occlude lead if not brought completely into solution. Perchloric acid in conjunction with nitric acid may be used to destroy organic matter. Perchloric acid very low in lead is on the market. The following simple digestion procedure is suitable for plant materials<sup>32</sup> and should be applicable to other materials of organic origin, if necessary with some modification in details.

### ¶ Procedure<sup>33</sup>

Transfer 4-5 g. of sample to a 400 ml. Pyrex beaker, add 10 ml. of concentrated nitric acid, cover with a watch glass, and heat gently until any vigorous initial action has subsided. Heat to boiling and boil until the contents are nearly dry. Add 10 ml. of 1:1 nitric acid and 10 ml. of 70 per cent perchloric acid. Heat to gentle boiling and maintain at this tem-

<sup>31</sup> If there is a possibility of tin being present, ignite in a porcelain crucible, transfer the residue to a platinum crucible and hydrofluorize.

<sup>32</sup> J. F. Giesecking, H. J. Snider, and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **7**, 185 (1935); for a similar procedure see H. W. Gerritz, *ibid.*, **7**, 167 (1935).

<sup>33</sup> See also p. 318.

perature until all organic material has been removed from the sides of the beaker and the liquid has become practically colorless. Remove the beaker from the heat, cool for a few minutes, and wash any salts on the cover glass into the beaker. Evaporate the solution just to dryness, add 5 ml. of 1:1 hydrochloric acid and 10 ml. of water, and warm until all soluble material has been brought into solution. If necessary, filter off the silica, hydrofluorize the ignited residue, etc. as described on p. 299. Determine lead in the solution, or an aliquot of it, according to the general procedure, p. 285. If a clear solution cannot be obtained when the citrate solution is made ammoniacal, isolate lead as the sulfide (see p. 299).

**Procedure in the Presence of Tin.**—If tin is present in more than minute amounts it will be converted into insoluble metastannic acid in the ashing or acid digestion and will cause loss of lead by occlusion. Most of the precipitated tin can be brought into solution and volatilized as follows.<sup>34</sup> Add 15 ml. or more of concentrated hydrobromic acid to the ash or the evaporation residue in the acid digestion (line 4, above) and heat on the steam bath. If nitrates were used in the ashing there will be an evolution of bromine, and the solution should finally be boiled to expel all of it. All the nitrate must be reduced. When the ash or the salts have been dissolved, examine the solution for insoluble metastannic acid. If a residue remains, add 50 to 100 mg. of pure finely granulated tin (*e.g.* prepared from U.S. Bureau of Standards Sample No. 42B, containing 0.0035 per cent lead) and boil gently until it is dissolved. This treatment should clear the solution. Next add 10 ml. or more of 60 per cent perchloric acid and a few milliliters of hydrobromic acid-bromine mixture (100 ml. redistilled 40 per cent HBr + 15 ml. liquid Br<sub>2</sub>). Evaporate to fumes of perchloric acid, adding small portions of hydrobromic acid-bromine totaling 15 ml. in the interval. When complete volatilization of the tin and the bromine has been effected, cool, and dissolve the contents of the vessel in the minimum volume of hot water. Continue with the determination as described above. The quantity of lead introduced from the metallic tin, hydrobromic acid-bromine, and perchloric acid must be found by running a blank.

<sup>34</sup> *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists*, 5th ed., 1940, p. 404.

## CHAPTER XXV

### LITHIUM

Traces of lithium are best determined spectrographically, although amounts greater than 10  $\gamma$  can be determined fairly satisfactorily by the colorimetric method described below under IIA. Separation from other metals is required.

#### I. Separations

The solubility of lithium chloride in a variety of organic solvents enables it to be separated without difficulty from the other alkali metal chlorides. The writer has had good success with the Palkin method,<sup>1</sup> in which sodium and potassium chlorides are precipitated from a small volume of aqueous solution by the addition of alcohol and ether (see further below, p. 302). Acetone should also be useful in such procedures. From magnesium, lithium is best separated by precipitation of the former with 8-hydroxyquinoline in ammoniacal solution. Many other metals are precipitated at the same time. The separation of calcium is effected by oxalate precipitation, but the coprecipitation of lithium with calcium oxalate necessitates one or more reprecipitations. Whether lithium in small amounts can be determined colorimetrically in silicates remains to be seen. The well-known tendency of lithium to be retained in the residue and the precipitates in the J. Lawrence Smith decomposition method may give rise to difficulties.

#### II. Methods of Determination

##### A. POTASSIUM FERRIC PERIODATE METHOD

Lithium solutions yield the slightly soluble salt  $\text{LiKFeIO}_6$  when treated with potassium ferric periodate in potassium hydroxide solution.<sup>2</sup> The precipitate may be washed with potassium hydroxide solution and dissolved in dilute acid, in which iron can be determined colorimetrically and lithium found from the Fe:Li ratio. Calcium and magnesium are precipitated by the reagent and give high results even when present in very small amounts. Sodium forms a sparingly soluble salt with the reagent, although low concentrations of the element do not yield a precipitate. Unfortu-

<sup>1</sup> S. Palkin, *J. Am. Chem. Soc.*, **38**, 2326 (1916).

<sup>2</sup> O. Procke and A. Slouf, *Collection Czechoslov. Chem. Commun.*, **11**, 273 (1939). These authors describe a volumetric method for the determination of lithium based on this precipitation.

nately sodium is strongly coprecipitated and difficulty is therefore usually encountered from the sodium present as impurity in the potassium hydroxide used in preparing the precipitant. The results given in Table 44 were obtained by the use of a reagent prepared from potassium hydroxide containing 0.25 per cent sodium (0.43 per cent sodium hydroxide). The positive error, which is relatively great for amounts of lithium of the order 0.01 mg., is believed to be due largely to coprecipitated sodium. If a standard curve is constructed, the presence of a small amount of sodium in the reagent does no great harm.

The iron in the solution of the dissolved triple periodate is conveniently determined by the thiocyanate method, but it is necessary to remember that the ferric thiocyanate color fades with time, especially on exposure to light.

#### Special Solutions

*Potassium ferric periodate reagent.* Add slowly with stirring 12 ml. of 0.10 *M* ferric chloride in 0.2 *N* hydrochloric acid to a mixture of 10 ml. of 2 *N* potassium hydroxide (reagent grade containing less than 0.25 per cent sodium) and 40 ml. of water in which has been dissolved 2.3 g. of potassium paraperiodate. Dilute to 100 ml. with 2 *N* potassium hydroxide. Filter the solution if it is not clear and keep it in a paraffin-lined bottle.

*Standard iron solution.* Prepare a solution containing 0.100 mg. of ferric iron and 0.59 mg. of potassium periodate per milliliter in 0.5 *N* hydrochloric acid.

*Standard lithium solution,* 0.01 per cent. This may be prepared by dissolving dried lithium carbonate in a slight excess of hydrochloric acid, or ignited lithium sulfate in water ( $\text{Li}_2\text{CO}_3/2 \text{ Li} = 5.32$ ,  $\text{Li}_2\text{SO}_4/2 \text{ Li} = 7.92$ ).

#### ¶ Procedure<sup>3</sup>

**Separation of Lithium from Sodium and Potassium.**—The sample solution may conveniently contain from 20 to 100  $\gamma$  of lithium. The alkali metals must be present as the chlorides and other metals must be absent. Evaporate the solution to dryness and dissolve the salts in a minimum volume of water (0.5 to 0.6 ml. for 200 mg. of the chlorides). Add 7 or 8 ml. of absolute ethyl alcohol and 20 ml. of anhydrous ether, stir the mixture well, and allow to stand for 5 minutes. Filter the solution through a small dry filter crucible and wash the salts with 5 ml. of a 1:4 alcohol and ether mixture. Evaporate the combined filtrate and washings to dryness in a small beaker.

**Precipitation and Determination of Lithium.**—Dissolve the residue of lithium chloride in a drop or two of water followed by 1 ml. of 1 *N* potassium hydroxide. Heat the solution to 90°–100° and add 2.0 ml. of potassium ferric periodate reagent which has been heated to boiling. Keep the

<sup>3</sup> E. B. Sandell, unpublished work.

mixture at 90°–100° for 5 minutes with occasional stirring, and then cool to room temperature by immersing the vessel in cold water for about 5 minutes. Filter through a small porous porcelain filter crucible and wash with four 0.75 to 1 ml. portions of 1 *N* potassium hydroxide solution.

Dissolve the precipitate in 10 ml. of cold 1 *N* hydrochloric acid, dilute the solution to exactly 25 ml. with water, transfer 5 ml. of the mixed solu-

TABLE 44

COLORIMETRIC DETERMINATION OF LITHIUM AFTER PRECIPITATION AS  $\text{LiKFeIO}_6$ 

Lithium calculated from the iron content of the precipitate by use of the theoretical factor  $\text{Li/Fe} = 0.124$ . The potassium hydroxide used in preparation of precipitant contained 0.25 per cent sodium.

Addition	Li taken $\gamma$	Li found $\gamma$
	5.0 <sup>a</sup>	6.8
	5.0 <sup>a</sup>	7.0
	10	13
	10	14
	20	24
	20	22
	50	55
	50	55
	100	107
	100	105
	100	105
0.5 mg. Na	20	26.5
0.5 mg. Na	50	59
0.5 mg. Na	100	108
1.0 mg. Na	0	0
0.2 mg. Ca, 0.2 mg. Mg	50	87
200 mg. Na <sup>b</sup>	20	25
200 mg. Na <sup>b</sup>	50	55
160 mg. Na <sup>b</sup>	100	100
100 mg. Na, 100 mg. K <sup>b</sup>	20	24
100 mg. Na, 100 mg. K <sup>b</sup>	50	50

<sup>a</sup> 0.5 ml. of 1 *N* potassium hydroxide and 1.0 ml. of reagent used instead of double these volumes as in the other determinations.

<sup>b</sup> Ether-alcohol separation of lithium.

tion to a 25 ml. volumetric flask, and add water to make the volume approximately 20 ml. Add 3 ml. of 2 *M* potassium thiocyanate solution, make up to 25 ml. with water and obtain the extinction of the solution at once (*cf.* p. 268). Instead of obtaining the amount of lithium from the theoretical factor  $\text{Li/Fe} = 0.124$ , it is preferable, especially if the sodium content of the potassium hydroxide solution is not known, to obtain it from a standard curve prepared by carrying known amounts of lithium

through the procedure. If a Duboscq colorimeter is used, the comparison solution may contain from 0.5 to 1.5 ml. of the standard iron solution together with 2 ml. of 2 *N* hydrochloric acid in a final volume of 25 ml.

#### B. STEARATE METHOD (TURBIDIMETRIC)<sup>4</sup>

An amyl alcohol solution of ammonium stearate added to a solution of lithium chloride in amyl alcohol produces a finely divided precipitate of lithium stearate which may be estimated turbidimetrically. The sensitivity of this method is somewhat smaller than that of the method described under IIA, but the accuracy is comparable. Calcium and magnesium must be absent.

##### Reagent

*Ammonium stearate.* Dissolve 2 g. of stearic acid in 100 ml. of ether, and pass dry ammonia into the solution until no further precipitation takes place, adding ether to replace that lost by evaporation. Allow the ether to evaporate and dissolve 2 g. of the residue in 100 ml. of warm (<50°) amyl alcohol. The solution must be prepared fresh because it becomes useless in the course of a few days.

##### ¶ Procedure

To 2.0 ml. of amyl alcohol containing 0.05 to 0.5 mg. of lithium as chloride,<sup>5</sup> add 5.0 ml. of ammonium stearate solution. At the same time add 5.0 ml. of the stearate solution to a series of standards, in identical tubes, containing 0.05, 0.075, . . . 0.5 mg. of lithium as chloride in 2.0 ml. of amyl alcohol. The reagent must be added at the same speed to all the solutions. Stopper the tubes, allow to stand for 30 minutes, then shake the contents and compare in the usual way. A filter photometer may be used to advantage in determining the concentration of the suspension from the amount of light transmitted (*cf.* p. 69).

<sup>4</sup> E. R. Caley, *J. Am. Chem. Soc.*, **52**, 2755 (1930).

<sup>5</sup> Lithium chloride may be separated from the other alkali metal chlorides by extraction with amyl alcohol according to the method of Gooch (see W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*. Wiley, New York, 1929), but better by the alcohol-ether method (p. 302). For the use of 2-ethyl hexanol in the separation of lithium from sodium and potassium, see E. R. Caley and H. D. Axilrod, *Ind. Eng. Chem., Anal. Ed.*, **14**, 242 (1942). This solvent can be substituted for amyl alcohol in the procedure described above.

## CHAPTER XXVI

### MAGNESIUM

#### I. Separations

Ferric iron, aluminum, etc. may be separated from magnesium by double ammonia precipitation in the presence of an ammonium salt. Phosphate is separated at the same time if sufficient iron or aluminum is present. Manganese may be precipitated with ammonium sulfide; zinc, nickel, cobalt, etc. are also precipitated. The usual double precipitation with oxalate serves to remove calcium, if it is present in quantities sufficiently large to interfere. When traces of magnesium are to be determined in calcium salts, a strong solution of the latter is treated with calcium oxide (about 0.2 g. of freshly ignited CaO for 100 ml. of neutral solution) to precipitate magnesium hydroxide; if necessary the calcium in the precipitate can be separated by the oxalate method.<sup>1</sup>

Separations with 8-hydroxyquinoline may at times be useful. For example, in a sodium tartrate-sodium hydroxide solution, magnesium but not aluminum is precipitated by hydroxyquinoline. See further p. 310.

A method of separation that should be borne in mind as being useful for traces of magnesium in certain materials is the one based on the solubility of magnesium chloride in amyl alcohol, ether-alcohol, and other organic solvents (*cf.* Lithium, p. 301).

#### II. Methods of Determination

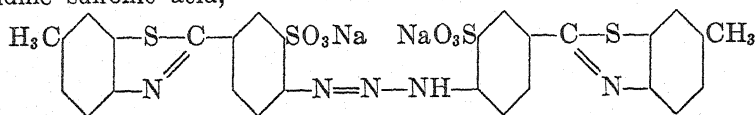
The direct colorimetric determination of magnesium is based on the formation of a lake of magnesium hydroxide with a dye such as Titan yellow or quinalizarin, and the indirect determination on the precipitation of magnesium 8-hydroxyquinolate, whose amount may be found in various ways from its hydroxyquinoline content. Both methods require the absence of most of the other metals. The Titan yellow method is in general to be preferred. It is very sensitive, easy to carry out, and may be applied in the presence of relatively much calcium, but it requires the absence of any appreciable amount of ammonium salts.

##### A. TITAN YELLOW METHOD

When magnesium hydroxide is precipitated with sodium hydroxide in the presence of various organic dyestuffs, the latter are adsorbed on the

<sup>1</sup> J. C. Hostetter, *J. Ind. Eng. Chem.*, **6**, 392 (1914). The solubility of magnesium hydroxide in 100 ml. of 10 per cent calcium chloride under the conditions of the separation is thought to correspond to less than 0.2 mg. MgO.

precipitate with a change in color. Since magnesium hydroxide is very slightly soluble in an excess of sodium hydroxide and the color intensity of the lake or the adsorption body is great, a very sensitive reaction can be obtained in this way. Titan yellow, the sodium salt of dehydrothio-*p*-toluidine sulfonic acid,



is a suitable color reagent.<sup>2</sup> It gives a red color with magnesium in sodium hydroxide solution ( $\text{pH} > 12$ ) and a yellow-brown color in the absence

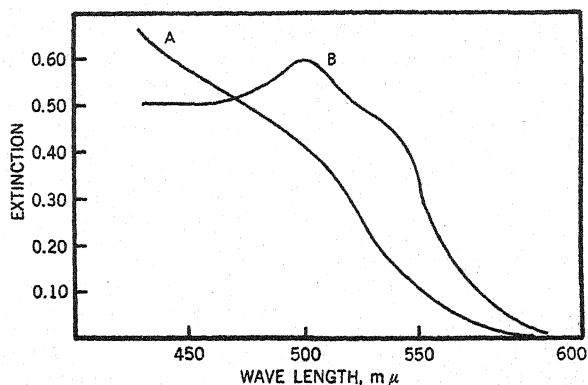


Fig. 40.—Absorption curves of (A) Titan yellow in sodium hydroxide solution, and (B) Titan yellow + magnesium in sodium hydroxide solution. (Based on curves given by Ginsberg, *loc. cit.*)

of magnesium. Fairly stable colloidal suspensions of the lake can be obtained if the magnesium concentration is kept below 3 or 4 parts per million, and the fading of the color is prevented by the presence of hydroxylamine hydrochloride. An equilibrium exists between the dyestuff and the lake, and the lake formation follows the simple laws of adsorption.<sup>3</sup> Beer's law holds only over a narrow range in which there is a sufficiently large excess of reagent (Fig. 41). Addition of a protective colloid is not necessary.

The reaction is subject to interference from many metals.<sup>4</sup> Some of the metal hydroxides (*e.g.* cadmium) adsorb Titan yellow and produce more or less of a color change. Certain metals giving hydroxides soluble in an excess of sodium hydroxide, particularly aluminum and tin, interfere seri-

<sup>2</sup> I. M. Kolthoff, *Biochem. Z.*, **185**, 344 (1927).

<sup>3</sup> H. Ginsberg, *Z. Elektrochem.*, **45**, 829 (1939).

<sup>4</sup> E. B. Otto and C. E. Otto, *Ind. Eng. Chem., Anal. Ed.*, **13**, 65 (1941).



ously by diminishing the intensity of the magnesium color. Even as little as 4 parts per million of aluminum will reduce the color intensity. This interference no doubt results from the adsorption of aluminate or stannate on the magnesium hydroxide, with a resulting decrease in the adsorption of Titan yellow.

In the procedure given below,<sup>5</sup> ammonium ion up to a concentration of 500 parts per million does not interfere. Phosphate ion destroys the color when present in excess of 100 parts per million. Calcium may be present in amounts up to about 100 parts per million. Sucrose is used to minimize the effect of calcium, which otherwise tends to deepen the color given by magnesium.

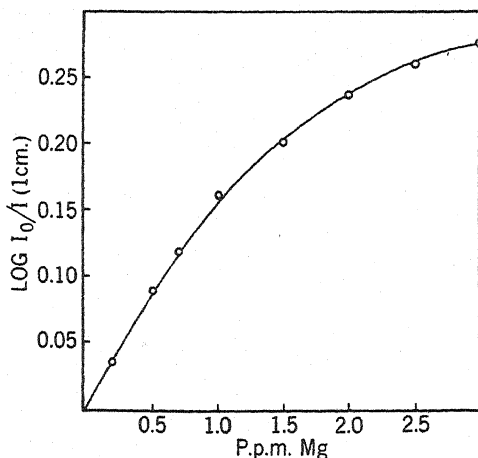


Fig. 41.—Determination of magnesium with Titan yellow (Wratten green filter No. 58). Curve constructed from data given by Gillam (*loc. cit.*).

#### Special Solutions

*Titan yellow A*, 0.05 per cent aqueous solution.

*Hydroxylamine hydrochloride*, 5 per cent aqueous solution.

*Sucrose*, 5 per cent solution in water.

*Sodium hydroxide*, 1 *N*.

*Standard magnesium solution*, 0.01 per cent. This is most conveniently prepared by dissolving pure magnesium metal in a slight excess of hydrochloric acid.

#### ¶ Procedure

If necessary, separate iron, aluminum, phosphate, etc. in the usual way by a double precipitation with ammonium hydroxide, and calcium with

<sup>5</sup> W. S. Gillam, *Ind. Eng. Chem., Anal. Ed.*, **13**, 499 (1941). For other procedures see A. D. Hirschfelder and E. R. Serles, *J. Biol. Chem.*, **104**, 635 (1934); E. E. Ludwig and C. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **14**, 895 (1942); C. Urbach and R. Baril, *Mikrochemie*, **14**, 343 (1934); V. G. Haury, *J. Lab. Clin. Med.*, **23**, 1079 (1938).

oxalate if it is present in quantity ( $\text{Ca/Mg} > 50$ ). (If other metals such as manganese, zinc, copper, etc. are present in more than traces they must be separated by appropriate methods.) Evaporate the filtrate to dryness if ammonia precipitation has been made, and ignite the residue gently to expel ammonium salts. Moisten the residue with a few drops of 1:1 hydrochloric acid, warm, add water and dilute to volume in a volumetric flask of suitable size.

Pipet into a 50 ml. volumetric flask an aliquot of such size that the final magnesium concentration will not exceed 3 p.p.m. and will preferably be greater than 0.2 p.p.m. Add successively 5 ml. of sucrose solution (this may be omitted if calcium has been separated or very little is present), 1 ml. of hydroxylamine hydrochloride, and 1.00 ml. of Titan yellow solution. Dilute to 30 or 40 ml. and add 5 ml. of sodium hydroxide while swirling the solution. Make up to the mark with water, mix and transfer the suspension to a suitable absorption cell. Use a green filter having a transmission maximum at or near 550  $m\mu$  in determining the extinction. The reference cell may be filled with water or Titan yellow-sodium hydroxide solution as preferred. The color intensity should not change appreciably in the course of an hour, but it is preferable to determine the extinction of the solution soon after the lake has been formed.

#### B. QUINALIZARIN METHOD

In sodium hydroxide solution, quinalizarin (p. 101) yields a blue lake with magnesium hydroxide; quinalizarin alone gives a violet solution in the presence of alkali. A procedure for the determination of magnesium with this reagent has been described by Thiel and van Hengel;<sup>6</sup> it is given below. Separation of magnesium from most of the other elements is required before the method can be applied. Beryllium gives a blue color with quinalizarin in strongly basic solution (p. 153), as do also the rare earth metals, zirconium, and thorium (p. 374).

#### Special Solutions

*Gum arabic*, 5 per cent aqueous solution prepared from the magnesium-free substance.

*Quinalizarin*, 0.01 per cent in 96 per cent ethyl alcohol.

#### ¶ Procedure

Transfer the neutral or weakly acid sample solution, containing up to 0.3 mg. of magnesium, to a 50 ml. volumetric flask. Add 5 ml. of gum arabic (this need not be added for low magnesium concentrations), 5 ml. of quinalizarin, and sufficient water to make the volume 35–40 ml. Then

<sup>6</sup> A. Thiel and E. van Hengel, *Ber.*, **71B**, 1157 (1938).

add 5 ml. of 2 *N* sodium hydroxide and dilute to volume. Determine the extinction at 600  $m\mu$ . The measurement should be made soon after mixing, since the excess quinalizarin is not stable in the basic medium; the color of the magnesium lake is more stable.

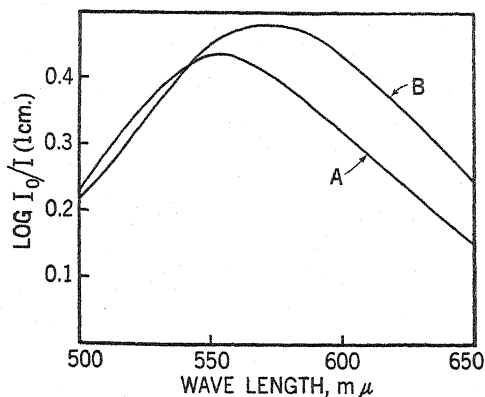


Fig. 42.—Absorption curves of (A) 1 mg. quinalizarin in 100 ml. 0.2 *N* sodium hydroxide, and (B) 1 mg. quinalizarin + 0.2 mg. magnesium in 100 ml. 0.2 *N* sodium hydroxide. (After Thiel and van Hengel.)

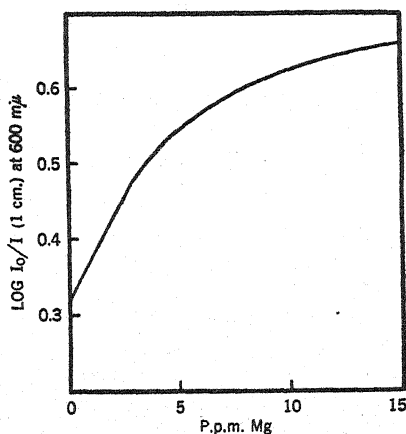


Fig. 43.—Determination of magnesium with quinalizarin (1 mg. in 100 ml.). (After Thiel and van Hengel.)

### C. 8-HYDROXYQUINOLINE AND OTHER METHODS

Many procedures have been described for the colorimetric determination of magnesium after precipitation as 8-hydroxyquinolate in ammoniacal

solution. The hydroxyquinoline in the precipitate may be determined with Folin's phenol reagent, with ferric iron in acetic acid or very dilute hydrochloric acid (blue-green color due to ferric hydroxyquinolate),<sup>7</sup> or by conversion into an azo dye by the use of diazobenzene sulfonic acid.<sup>8</sup> Since 8-hydroxyquinoline gives precipitates with most metals in ammoniacal solution, these must be completely separated before the method can be applied. Small amounts of aluminum, ferric iron, copper, and various other metals can be precipitated with 8-hydroxyquinoline in acetic acid-acetate medium. Calcium, unless present in very low concentrations, must be separated as the oxalate, for calcium quinolate is not very soluble and is likely to come down with the magnesium precipitate. According to Sideris (*loc. cit.*) it is possible to separate magnesium from aluminum, iron, man-

TABLE 45  
DETERMINATION OF MAGNESIUM BY THE TITAN YELLOW METHOD

Mg taken <sup>a</sup> mg.	Ca present mg.	Mg found mg.
0.025		0.025
0.050		0.050
0.100		0.102
0.025	5	0.024
0.025	10	0.018
0.050	1	0.052
0.050	2.5	0.052
0.050	5	0.045
0.050	10	0.038
0.100	5	0.100 <sup>b</sup>
0.100	6.5	0.100
0.100	10	0.083

<sup>a</sup> Final volume 50 ml.

<sup>b</sup> When transmittancy was determined after 75 minutes instead of soon after mixing, 0.102 mg. was found.

ganese, lead, and zinc by precipitating the hydroxyquinolates of all these metals in ammoniacal solution and then extracting the last named quinolates with chloroform; the undissolved magnesium quinolate may be filtered off. This separation procedure appears promising, but there are not sufficient data available to demonstrate its reliability for traces of magnesium.

Other methods which have been used for determining small amounts of magnesium include: precipitation as magnesium ammonium phosphate

<sup>7</sup> See, for example, W. S. Hoffman, *J. Biol. Chem.*, **118**, 37 (1937); L. Gerber, R. I. Claassen, and C. S. Boruff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 658 (1942); C. P. Sideris, *ibid.*, **12**, 232 (1940). The latter author extracts the ferric quinolate with chloroform and dilutes to volume with butyl alcohol.

<sup>8</sup> F. Alten, H. Weiland, and H. Loofman, *Angew. Chem.*, **46**, 668 (1933).

and the determination of phosphate in the precipitate by one of the numerous colorimetric methods for phosphorus; formation of an orange lake with curcumin in basic solution in the presence or absence of phosphate;<sup>9</sup> nephelometric or turbidimetric procedures based on the formation of suspensions with trisodium phosphate or ammonium ferrocyanide.

Directions for the determination of magnesium by the 8-hydroxyquinoline method follow. The washed quinolate precipitate is dissolved in dilute hydrochloric acid and the concentration of the hydroxyquinoline is found from the intensity of the color produced by the addition of ferric chloride, essentially according to the procedure of Hoffman (*loc. cit.*).

### Reagents

*8-Hydroxyquinoline*, 5 per cent solution in 2 *N* acetic acid. This solution is stable for months.

*Ammonium hydroxide wash solution*, 1:25. When very small amounts of magnesium are to be determined it is preferable to saturate this solution with magnesium hydroxyquinolate.

*Ferric chloride solution*, 5 per cent  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 0.1 *N* hydrochloric acid.

*Hydrochloric acid*, 0.01 *N*.

### Procedure

The sample solution, containing up to about 100  $\gamma$  of magnesium, should have a volume in the neighborhood of 5 ml. A small beaker (10 or 15 ml.) is a convenient precipitation vessel. To the neutral or slightly acid solution add 0.2 ml. of 8-hydroxyquinoline and heat to 70° or 80°. While stirring, add 1:1 ammonium hydroxide until the solution is basic and then an excess of 5 or 10 drops. Set the solution aside for an hour without further heating. Filter, preferably using a filter stick (see p. 367), and wash carefully with about four small (0.5 ml.) portions of the ammonia wash solution.

Dissolve the precipitate in 1 ml. of hot 0.01 *N* hydrochloric acid and wash the beaker and filter stick with small portions of warm water. Cool the solution and transfer it to a 10 or 25 ml. volumetric flask. Add 0.10 ml. of the ferric chloride solution and dilute to volume with water. Obtain the extinction of the solution with an orange filter or light of 650  $m\mu$  wave length. The standard curve is obtained by carrying appropriate amounts of magnesium through the whole procedure. The relationship between magnesium concentration and color intensity is linear or nearly so.

<sup>9</sup> W. E. Thrun, *Ind. Eng. Chem., Anal. Ed.*, **4**, 426 (1932).

## CHAPTER XXVII

### MANGANESE

#### I. Separations

For isolating manganese from very dilute solutions or for separating it from substances such as chloride which interfere in the colorimetric determination, precipitation with sodium hydroxide is useful. There will generally be sufficient oxygen present in the solution to oxidize the precipitate to hydrous manganese dioxide which is highly insoluble. A few milligrams of ferric salt may be added to give ferric hydroxide which will gather the manganese. The sodium hydroxide should be added to the sample solution at room temperature, the mixture stirred for a minute or two, and then heated to boiling to coagulate the precipitate. The latter, after being washed, is dissolved in dilute sulfuric or nitric acid to which a little sulfite has been added, and the periodate method applied.

From chromium, as well as from vanadium, molybdenum and tungsten, manganese can be separated by treatment with sodium peroxide in alkaline solution (or by fusion with sodium peroxide or carbonate, followed by heating with alcohol to reduce manganate).

The separation of manganese from iron (rarely required) can be accomplished by extracting ferric chloride with ether from 1:1 hydrochloric acid. Before manganese can be determined colorimetrically in the aqueous phase, it must be separated from the chloride as already described, or chloride removed by evaporation with sulfuric acid.

#### II. Methods of Determination

##### A. THE PERMANGANATE METHOD

The colorimetric determination of manganese by oxidation to permanganate in acid solution is so sensitive and specific that it leaves little to be desired. Although a number of reagents such as lead dioxide, sodium bismuthate, and persulfate (with silver as catalyst) may be used to oxidize manganous ion to permanganate in acid medium, potassium or sodium periodate is by far the best reagent for the purpose.<sup>1</sup>

The reaction  $2 \text{Mn}^{++} + 5 \text{IO}_4^- + 3 \text{H}_2\text{O} \rightarrow 2 \text{MnO}_4^- + 5 \text{IO}_3^- + 6 \text{H}^+$  proceeds rapidly in a hot solution containing nitric or sulfuric acid. Since ferric periodate is slightly soluble in nitric acid, either sulfuric or phosphoric acid must be present if the solution contains much iron. Phosphoric acid

<sup>1</sup> H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, **39**, 2366 (1917).

decolorizes ferric iron by complex formation, and its presence is desirable in any case since it prevents possible precipitation of periodates or iodates of manganese. Unless the amount of manganese is very small the concentration of acid can be increased considerably over the minimum required to prevent precipitation without ill effect, and as a matter of fact the speed of oxidation of manganese is increased when the sulfuric acid concentration is increased above 3.5 *N*. It has been shown,<sup>2</sup> however, that with low concentrations of manganese (a few micrograms in 10 ml.) the acidity should be less than that corresponding to 15 ml. of concentrated sulfuric acid per 100 ml. of solution, for above this the full color does not develop, or it fades and a yellow tint is developed. Richards<sup>2</sup> recommends an acidity of 2 *N* (5–6 per cent by volume of sulfuric acid) for small amounts of manganese, because at this acidity the oxidation is more rapid than at 3.5 *N* (10 per cent sulfuric acid by volume).

Reducing substances reacting with periodate or permanganate must be removed or destroyed before the periodate oxidation is attempted. Although chloride in small amount can be oxidized by periodate, it is safer to remove it by evaporation with sulfuric acid, especially if the sample contains only a small amount of manganese. Ferrous iron, sulfite, nitrite, bromide, iodide, etc., and oxalate and other oxidizable organic anions may be removed or destroyed by evaporating the solution of the sample with nitric acid or a mixture of nitric and sulfuric acids. Among the anions not interfering may be mentioned arsenate, borate, fluoride, perchlorate, and pyrophosphate.

Foreign metals, with a few exceptions, do not interfere except when they are colored. The effect of copper, nickel, cobalt, etc. can be compensated by the use of an aliquot portion of the sample solution in the photometer reference cell or by the addition of a like amount to the comparison solution. For example, the determination can in the latter case be made by colorimetric titration (p. 43), the standard permanganate solution being added to a comparison solution containing the same amount of sample as the oxidized sample solution. Chromium (III) is oxidized to a greater or less extent by periodate; increasing the acidity decreases the amount of chromium oxidized. Cerium (III) is also oxidized by periodate in acid solution. Silver, lead, and mercury give no precipitates if sufficient acid is present, but bismuth and tin give turbidities even in strongly acid solutions.<sup>3</sup>

Beer's law holds closely for concentrations of manganese up to 150 mg. per liter at least. Variation in acid concentration and periodate excess do not affect the color intensity.

<sup>2</sup> M. B. Richards, *Analyst*, **55**, 554 (1930).

<sup>3</sup> J. P. Mehlig, *Ind. Eng. Chem., Anal. Ed.*, **11**, 274 (1939).

### Standard Manganese Solution

This is most easily prepared by dissolving pure (99.9 + per cent) electrolytic manganese metal in dilute nitric acid, boiling out oxides of nitrogen, and diluting to give a 0.01 per cent solution. If manganese metal is not available, the standard solution can be obtained by reducing potassium permanganate solution, standardized in the usual way, with a little sulfite after the addition of sulfuric acid, and then boiling out the sulfur dioxide.<sup>4</sup> The standard permanganate solution is obtained by suitably diluting the manganous solution and oxidizing with potassium periodate in the same way that the sample solution is oxidized.

### ¶ General Procedure

If the solution of the sample contains chloride, add sulfuric acid and evaporate to fumes of the latter. If ferrous iron and other oxidizable substances are present, boil with nitric acid, or add the latter before evaporation with sulfuric acid.

The solution, ready for analysis, should in the usual case (0.1–1 mg. of manganese present) contain 10 ml. of concentrated sulfuric acid or 15 to 20 ml. of nitric acid, and in addition 5 to 10 ml. of 85 per cent phosphoric acid, in a volume of 100 ml. However, if the amount of manganese present is of the order of a few micrograms make the solution 2 *N* in sulfuric acid. Add 0.3–0.4 g. of potassium metaperiodate, or an equivalent amount of any other alkali metal periodate, for each 100 ml. of solution, heat to boiling with stirring, and keep at or slightly below the boiling point for 5 to 10 minutes. Cool, dilute to volume if the comparison method requires, and make the color comparison or measurement in any convenient way. Permanganate solutions show maximum absorption at about 525  $\mu$ .<sup>5</sup>

The oxidized solution containing an excess of periodate is stable and may be kept many months without change, at least if stored in the dark.

### B. OTHER METHODS

Manganese in higher stages of oxidation (IV and VII) reacts with various organic compounds to give strongly colored oxidation products. *o*-Tolidine,<sup>6</sup> tetramethyldiaminodiphenylmethane,<sup>7</sup> and benzidine<sup>8</sup> are some of the reagents that have been used. These methods are unspecific since other strong oxidizing agents react similarly. The colors produced are not

<sup>4</sup> In many cases a standard solution obtained by weighing out a good grade of potassium permanganate crystals and reducing will serve the purpose. 2.88 mg.  $\text{KMnO}_4 = 1.00$  mg. Mn.

<sup>5</sup> In the presence of chromium (VI) determine the transmittancy at 575  $\mu$ ; at and above this wave length dichromate solutions absorb very slightly.

<sup>6</sup> L. Forman, *J. Am. Water Works Assoc.*, **21**, 1212 (1929).

<sup>7</sup> R. G. Harry, *J. Soc. Chem. Ind.*, **50**, 434T (1931).

<sup>8</sup> R. C. Stratton, J. B. Ficklen, and W. A. Hough, *Ind. Eng. Chem., Anal. Ed.*, **4**, 2 (1932); N. A. Clark, *ibid.*, **5**, 241 (1933). See also p. 317.



stable, although very intense so that as little as 0.1  $\gamma$  of manganese (VII) can be detected in 100 ml. when benzidine is used.

In basic solutions manganese (II) yields a brown-red color with formal-doxime and this has been made the basis of a quantitative method.<sup>9</sup> Iron and much phosphate interfere.

Manganese has been determined colorimetrically as pyrophosphato-manganic acid (violet color); the sensitivity is not great.<sup>10</sup>

### III. Applications of the Permanganate Method

#### A. SILICATE ROCKS

In silicate rocks manganese usually occurs in more than trace amounts ( $> 0.01$  per cent), and the following directions are intended for such quantities as are generally encountered.

##### ¶ Procedure

Transfer 0.5 g. of finely powdered sample to a large platinum crucible or a small platinum dish and add 5 ml. of 1:1 sulfuric acid and 3-4 ml. of hydrofluoric acid. Mix, and heat the vessel in a "radiator" or on a hot plate, carefully at first and then more strongly until fumes of sulfuric acid are given off. Cool, wash down the sides of the vessel with a little water, and add 2-3 ml. of dilute sulfuric acid and a few drops of nitric acid. Evaporate again to strong fumes of sulfuric acid. Add 10-15 ml. of water and warm until all soluble material has been brought into solution. Filter through a small filter paper and wash with hot water, keeping the total volume of the filtrate and washings below 50 ml. Add to the solution 3 ml. of concentrated sulfuric acid, 2 ml. of 85 per cent phosphoric acid and 0.3 g. of potassium periodate. Heat to boiling, keep at or just below the boiling point for 5 minutes, cool, and dilute the solution to 100 ml. or to a larger volume if the color intensity is strong. After mixing, determine the transmittancy of the solution or compare against a similar standard.

#### B. IRON ORE

##### ¶ Procedure

Decompose a suitable weight of sample (containing not more than 5 mg. of manganese) with hydrochloric acid. Filter off any residue on paper, ignite and heat with hydrofluoric and sulfuric acids; evaporate the mixture to fumes of sulfuric acid. Dissolve the residue in hydrochloric acid and add to the main solution.

<sup>9</sup> C. P. Sideris, *Ind. Eng. Chem., Anal. Ed.*, **9**, 445 (1937); **12**, 307 (1940). G. H. Wagenaar, *Pharm. Weekblad*, **75**, 641 (1938).

<sup>10</sup> E. S. Tomula and V. Aho, *Ann. Acad. Sci. Fennicae*, **A 52**, No. 4 (1939); **A 55**, No. 1 (1940).

Add 5–10 ml. of sulfuric acid and 20 ml. of nitric acid to the solution of the sample and evaporate until fumes of sulfuric acid appear; all chloride should thus be removed. Then add approximately 50 ml. of water, and heat until all ferric sulfate has been brought into solution. Filter off any suspended material, add 5 to 10 ml. of 85 per cent phosphoric acid to the filtrate and mix. The solution should be practically colorless. Add 0.3 g. potassium or sodium paraperiodate, heat to boiling and keep at or near this temperature for 5 minutes. If there is any delay in the appearance of the permanganate color the presence of chloride is indicated and more periodate should be added to oxidize any small amounts of the latter. Dilute the solution to a suitable volume (usually 250 ml.) depending upon the color intensity, and compare against a standard solution or determine the transmittancy.

#### C. STEEL

##### ¶ Procedure

Dissolve 0.5–1 g. of sample in 50 ml. of 1:3 nitric acid and boil for a few minutes to expel oxides of nitrogen. Cautiously add 1 g. of ammonium persulfate, and boil 10–15 minutes to oxidize carbon compounds and destroy the excess of persulfate. If a color of permanganate is visible or oxides of manganese separate, add a few drops of sulfur dioxide solution or dilute sodium sulfite solution to destroy the color and to clear the solution. Then boil for 5 minutes to expel sulfur dioxide. Dilute to about 100 ml., add 10 ml. of 85 per cent phosphoric acid and 0.5 g. of potassium periodate, heat to boiling, and keep at the boiling point for 5 minutes. Cool the solution and dilute to 250 ml. (or a smaller or larger volume as the color intensity may demand). Determine the transmittancy of the solution or compare against a standard solution. The standards for comparison or for the construction of the reference curve should preferably contain about the same amount of iron as the sample solution itself. When a photometer is used, any color due to nickel, cobalt, etc. as well as any faint color of iron may be compensated by using an aliquot of the sample solution, not oxidized with periodate but otherwise treated the same as the sample, in the reference cell of the instrument. When chromium is present, the extinction of the solution should be obtained at 575  $m\mu$  as already mentioned.

#### D. WATER

##### ¶ Procedure

Acidify 50–100 ml. of water with 3–4 drops each of sulfuric and nitric acids and evaporate to dryness (a Pyrex beaker may be used). Then determine manganese by the general procedure (p. 314), keeping the volumes small.

For isolating very small amounts of manganese in water (as little as 10  $\gamma$  per liter) use the sodium hydroxide precipitation method with a little ferric iron as a collector (p. 312). The precipitate of ferric hydroxide, calcium carbonate, etc. may be dissolved in dilute nitric acid containing a little sulfite to reduce higher oxides of manganese. By applying the general periodate procedure in a volume of 5–10 ml. a few micrograms of manganese can easily be determined.

### E. BIOLOGICAL MATERIALS

Organic matter can be destroyed either by wet oxidation or by ashing. Ashing by ignition has some advantages when very low percentages of manganese are to be determined, since the volume of the final solution can be kept small and high sensitivity thus obtained. Under proper ashing conditions there is but little retention of manganese by silica remaining after treatment with acid (*cf.* Table 2 for some values for siliceous samples). A muffle furnace, not a burner, should be used for the ignition and the temperature should preferably be kept below 600° to preclude or minimize the formation of acid insoluble manganese silicates. Any manganese in the acid-insoluble material can be recovered by hydrofluorization or fusion with sodium carbonate.

Wet oxidation can be carried out by the usual methods. Directions are given below for oxidation with nitric and perchloric acids, and (for those wishing to avoid the use of perchloric acid) with nitric and sulfuric acids.

The permanganate method as described under II A is usually the most suitable one for determining manganese in the final solution. However, if only a small weight of sample is available a more sensitive indirect method based on the oxidation of benzidine by permanganate in nitric acid solution may be applied.<sup>11</sup> Sodium bismuthate is used to oxidize manganese (II) to permanganate and the transmittancy of the yellow-green solution of the oxidized benzidine is determined at 420  $m\mu$ .

### ¶ Procedures

**1. Ashing by Ignition.**<sup>12</sup>—Transfer 1 to 5 g. of sample (the latter amount for manganese contents of 10 p.p.m.) to a platinum or, less preferably, to a silica or porcelain dish. Char at a low temperature and then heat in a muffle furnace at 550–600° until a white ash is obtained. Moisten the ash with a few drops of concentrated hydrochloric acid, add a milliliter or two

<sup>11</sup>A. C. Wiese and B. C. Johnson, *J. Biol. Chem.*, **127**, 203 (1939).

<sup>12</sup> Among others, ashing by ignition has been used by D. R. K. Coleman and F. C. Gilbert, *Analyst*, **64**, 726 (1939); T. W. Ray, *J. Biol. Chem.*, **134**, 677 (1940); F. E. Read, *Analyst*, **64**, 586 (1939); and M. B. Richards, *Analyst*, **55**, 554 (1930).

of water, warm, and rinse the solution together with any insoluble material into a small Pyrex beaker. Add 1–2 ml. of 1:1 sulfuric acid and evaporate to thick fumes of sulfuric acid. (If much calcium is present omit the addition of sulfuric acid and evaporate to dryness two or three times with small portions of nitric acid.) Dilute with water to about 25 ml., warm, and if the solution contains suspended material filter through a small paper previously washed with hot 0.1 *N* sulfuric acid. Wash with a little dilute sulfuric acid. If the quantity of insoluble material is relatively large, or for the greatest accuracy in any case, ignite the paper and its contents in a platinum crucible. Add 1–2 ml. of hydrofluoric acid and a few drops of sulfuric acid and evaporate to fumes of the latter. Take up the residue in a little dilute sulfuric acid and add the clear solution to the main solution. Add 3 ml. each of concentrated sulfuric acid and 85 per cent phosphoric acid and dilute to about 75 ml. Then add 0.3 g. of potassium periodate, heat to boiling, and keep just below the boiling point for 10 or 15 minutes. Dilute to 100 ml. (or more if the color is strong) and find the extinction of the solution, or compare in a colorimeter against a suitable standard.

**2. Nitric-perchloric Acid Digestion.**<sup>13</sup>—Transfer 1 to 4 g. of sample to a 500 ml. Kjeldahl flask. Add 40 ml. of concentrated nitric acid and boil gently so that nearly all of the acid is evaporated in one-half hour; avoid charring the sample. Then add 13 ml. of 60 per cent perchloric acid and boil gently until white fumes appear. Reduce the heat and continue the digestion barely at the boiling point for 10–15 minutes. Cool, dilute with an equal volume of water, and filter through a sintered glass crucible or funnel. Wash with water and dilute the filtrate to about 75 ml. if necessary. Add 3 ml. of phosphoric acid and 0.3 g. of sodium or potassium periodate, heat to boiling, and keep slightly below the boiling point for 15 minutes. Cool and dilute to 100 ml. (or a larger volume if the color is strong). Obtain the extinction of the solution or compare against a standard solution in a colorimeter.

**3. Nitric-sulfuric Acid Digestion.**<sup>14</sup>—Transfer 1 to 5 g. of sample to a 500 ml. Kjeldahl flask, moisten with concentrated nitric acid, and add 5 to 10 ml. of concentrated sulfuric acid. After subsidence of any initial vigorous reaction, heat gently and cautiously add nitric acid in small (*ca.* 1 ml.) portions. When the color of the mixture begins to lighten, increase the heat and continue the addition of nitric acid until on evaporation to fumes of sulfuric acid a practically colorless solution is obtained. Add 1 g. of potassium persulfate, and dilute with an equal volume of water. Evaporate until fumes of sulfuric acid appear. Cool and transfer the solution

<sup>13</sup> J. W. Cook, *Ind. Eng. Chem., Anal. Ed.*, **13**, 48 (1941).

<sup>14</sup> D. R. K. Coleman and F. C. Gilbert, *Analyst*, **64**, 726 (1939).

to a 250 ml. Erlenmeyer flask with about 75 ml. of water. Boil for 5 minutes. If the solution is not entirely clear, filter it. If necessary dilute to 100-125 ml., then add 3 ml. of 85 per cent phosphoric acid and 0.3 g. of potassium periodate, and heat to boiling. Keep at or slightly below the boiling point for 10-15 minutes. Cool, dilute to a suitable volume, and obtain the transmittancy of the solution or compare against a suitable standard solution in a colorimeter.

## CHAPTER XXVIII

### MERCURY

#### I. Separations

In the absence of large quantities of metals yielding slightly soluble sulfides in acid solution, mercury may be isolated advantageously by precipitation with hydrogen sulfide. Copper sulfide is used as collector. The precipitate is dissolved in chlorine water, most of the excess chlorine is removed by aeration and the remainder by the addition of a reducing agent such as hydroxylamine hydrochloride. It is also possible to isolate mercury by allowing the solution ( $pH$  5-7) to flow slowly through an asbestos pad impregnated with cadmium sulfide.<sup>1</sup> In this way 98 per cent or more of the mercury in 200 ml. of solution containing 0.5  $\gamma$  of mercury can be recovered.

By the use of dithizone, mercury can be extracted from a mineral acid solution (*ca.* 1  $N$ )<sup>2</sup> and separated from such metals as lead, cadmium, zinc, and nickel which do not react appreciably with the reagent under these conditions. It is even possible to effect a separation from copper, if the copper-mercury ratio is not too unfavorable, by making use of fractional extraction, *i.e.*, shaking the acid solution with successive small portions of a dilute carbon tetrachloride or chloroform solution of dithizone until the color of the extracts changes from the orange of mercuric dithizonate to the red-violet of cupric dithizonate. More simply, copper can be extracted in acid medium containing bromide or iodide (together with a reducing agent such as sulfurous acid in the latter case), which prevent the reaction of mercury by complex formation.<sup>3</sup> If the aqueous solution is now made basic (or adjusted to  $pH$  6 if bromide is the complex forming agent), mercury can be extracted with dithizone. Mercury can be separated from small amounts of silver by first extracting both metals with dithizone and then shaking the extract with a dilute solution of a chloride or thiocyanate to decompose the silver dithizonate, while leaving the mercury in the organic solvent.

Another method for the isolation of traces of mercury, which has been

<sup>1</sup> A. E. Ballard and C. D. W. Thornton, *Ind. Eng. Chem., Anal. Ed.*, **13**, 893 (1941).

<sup>2</sup> At high acidities much chloride hinders the extraction of mercury. Complete extraction can still be obtained in 1  $N$  acid solutions which are 0.2  $N$  in chloride.

<sup>3</sup> In a variant procedure the carbon tetrachloride solution of copper and mercuric dithizonates is shaken with an acid bromide or iodide solution. Copper remains in the organic solvent phase, but mercury enters the aqueous layer. See p. 324.

used extensively by Stock<sup>4</sup> and coworkers involves electrolytic deposition of the metal on a copper wire, followed by volatilization by heating in a capillary tube. This method need rarely be applied when the final determination of mercury is made colorimetrically.

Certain types of inorganic material may simply be heated at a high temperature to expel the mercury present. Thus, to isolate mercury in rocks and minerals, a 20–100 g. sample is heated for several hours at 800° C. in a porcelain tube, while air is passed through it. The mercury in the issuing stream is condensed in a U-tube cooled with liquid air.<sup>5</sup>

The analyst engaged in the separation and determination of traces of mercury must bear in mind several sources of error that may vitiate the results. In the first place, mercury is by no means an infrequent contaminant of some reagents, in which however it occurs only in minute amounts. Attention may be called to its frequent presence in hydrochloric acid.<sup>6</sup> Mercury may also be present in filter paper, rubber stoppers, etc., especially if these have long been exposed to the atmosphere of the laboratory which may contain mercury vapor. Glassware should be well-rinsed with nitric acid and water before use. Mercury shows a great tendency to be adsorbed on glass. The adsorption is strongest from neutral solutions. However, even acidified solutions of mercury may undergo an appreciable change in concentration on standing, especially if they are very dilute. Adsorption is weakest on silica, but Pyrex ware is suitable for all but the most refined work.

The volatility of mercury and its compounds complicates the decomposition and preparation of the sample for analysis. Suitable precautions to prevent volatilization losses must be taken.

## II. Methods of Determination

### A. THE DITHIZONE METHOD

Divalent mercury reacts readily with excess dithizone in fairly acid medium (1 N in mineral acid) to yield the keto complex which is soluble in carbon tetrachloride or chloroform (orange color).<sup>7</sup> The mixed color method (p. 84) is the most suitable one for the determination of mercury

<sup>4</sup> A great deal of work has been done by A. Stock on the trace analysis of mercury, mostly by the micrometric method in which the diameter of the globule of the isolated mercury is measured. A list of the papers of Stock may be found in *Ber.*, **71**, 550 (1938). For the methods used see especially *Z. angew. Chem.*, **39**, 466, 791 (1926); **41**, 546 (1928); **42**, 429 (1929); **44**, 200 (1931); **46**, 62, 187 (1933); **47**, 641 (1934). *Ber.*, **67**, 122 (1934); **71**, 550 (1938); **72**, 1844 (1939).

<sup>5</sup> A. Stock and F. Cucuel, *Naturwissenschaften*, **22**, 390 (1934).

<sup>6</sup> The mercury in synthetic hydrochloric acid has its origin in the chlorine which has been obtained by electrolysis of sodium chloride with amalgam electrodes.

<sup>7</sup> Mercurous mercury gives a yellow solution under the same conditions.

with dithizone. Other metals reacting with dithizone in acid solution are copper, silver, gold, palladium, and divalent platinum. Small amounts of silver do not interfere if a sufficient concentration of chloride is present, but copper must be separated. Lead, zinc, nickel, cobalt, etc., do not interfere unless they are present in high concentrations, since the dithizonates of these metals have equilibrium constants that are much smaller than that of the mercuric complex. Bismuth in appreciable amounts may be expected to interfere to some extent since its dithizonate is stable in dilute acid solutions.

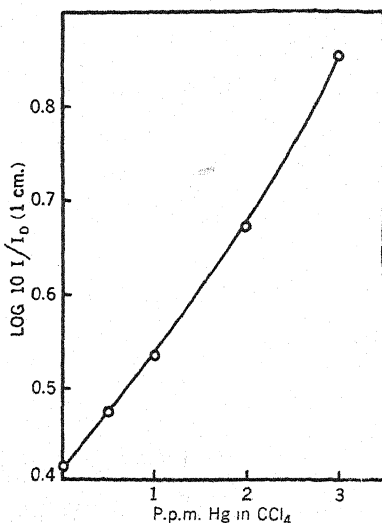


Fig. 44.—Determination of mercury (II) with dithizone by the mixed-color method (red filter).

Either a carbon tetrachloride or a chloroform solution of dithizone may be used in the mixed color method.

#### Special Solutions

*Dithizone*, 0.001 per cent (w/v) in analytical-reagent carbon tetrachloride.

*Standard mercury solution*, 0.100 per cent. Dissolve 0.1354 g. of mercuric chloride in 100 ml. of 1 *N* sulfuric acid. From this solution prepare by dilution a 0.001 or 0.002 per cent solution in 1 *N* sulfuric acid. The latter solution should preferably be prepared fresh every few days.

#### ¶ Procedure

The sample solution may contain up to 15  $\gamma$  of mercury (II) and should be about 1 *N* in sulfuric acid; the volume may be 5–50 ml. Add exactly 5 ml. of dithizone and shake for one minute. A mixed color should be ob-



tained. If not, add more dithizone and shake again. Dry the stem of the funnel with a roll of filter paper if necessary and transfer the carbon tetrachloride (which should be perfectly clear) to a suitable cell. Determine the transmittancy of the solution at either 500  $m\mu$  (absorption by mercuric dithizonate) or about 625  $m\mu$  (absorption by the excess dithizone). Make the measurement as rapidly as possible to avoid error due to change in transmittancy on exposure to light (p. 93). It is advisable to carry out all the operations in subdued daylight or artificial light.

#### B. THE DIPHENYLCARBAZONE METHOD

Diphenylcarbazone gives a slightly soluble blue-violet product with mercury salts, which under suitable conditions forms a colloidal suspension and makes a colorimetric determination possible. The nature of the blue product is not definitely known, but it may be a complex salt analogous to the compound that mercury (II) forms with dithizone. Diphenylcarbazide gives the same reaction as diphenylcarbazone because of its easy oxidizability to the carbazone by the oxygen of the air. The reaction is very sensitive, but is subject to many interferences. Diphenylcarbazone was used by Stock and others in determining minute amounts of mercury separated by distillation.

The use of diphenylcarbazide as a reagent for mercury was studied by Laird and Smith.<sup>8</sup> Since the dithizone method is much to be preferred to the diphenylcarbazide method, only a summary of the findings of these authors will be given here. The pH of the sample solution should be adjusted to  $4 \pm 0.3$  (acetic acid-sodium acetate buffer is suitable). The reagent is added in the form of a freshly-prepared 1 per cent solution in absolute alcohol. The intensity of color is independent of the amount of reagent added provided the ratio of reagent to mercury is 2:1 or greater. Beer's law is not strictly obeyed. Maximum color intensity is attained within 15 minutes, and no appreciable fading occurs in a period of several hours.

Electrolytes tend to flocculate the colored product. Nitrates and sulfates of the alkali metals and ammonium cause precipitation in less than an hour if the concentration of the salt is greater than 0.003 to 0.004 *N*. Flocculation is more rapid the higher the pH. At a pH greater than 6, flocculation occurs in a short time even in the absence of an electrolyte. Chloride reduces the color intensity seriously; a chloride concentration as low as 0.0001 *N* causes destruction of the color. Ammonium ion shows a slight tendency to reduce the color intensity. Many heavy metals, including iron and copper, interfere by giving colored products. Zinc interferes if present in an amount five times greater than that of mercury.

<sup>8</sup> F. W. Laird and Sister Alonza Smith, *Ind. Eng. Chem., Anal. Ed.*, **10**, 576 (1938).

The mercury compound may be extracted by carbon tetrachloride or chloroform.

### C. OTHER METHODS

Procedures for the determination of small amounts of mercury have been based on the formation of colloidal mercuric sulfide, colloidal iodo-mercurates of alkaloids such as strychnine (nephelometric), and a brown color with potassium iodide and ammonia. These methods are now of slight importance in trace analysis.

A very sensitive physical method may be based on the absorption of radiation of 253.7  $m\mu$  wave length by mercury vapor.<sup>9</sup> This principle has been applied not only in the determination of mercury vapor in air (p. 329), but also in the determination of traces of mercury which have been isolated as the sulfide. In the latter case the sulfide (collected on cadmium sulfide, p. 320) is volatilized into an absorption cell with quartz windows by heating at 550° and the absorption then measured.<sup>10</sup> Less than 0.1  $\gamma$  of mercury can be determined in this way.

## III. Applications of the Dithizone Method

### A. BIOLOGICAL MATERIALS

Two procedures are given below for the determination of traces of mercury in samples of biological origin. The first procedure is characterized by great simplicity and appears to give highly satisfactory results. The second procedure is more involved and requires a considerably longer time for its performance, but it also gives satisfactory recoveries of mercury.

#### 1. The Method of Laug and Nelson<sup>11</sup>

The salient feature of this method is the separation of mercury from copper by shaking the chloroform solution of the dithizonates with an acid potassium bromide solution. Mercury is thus transferred to the aqueous phase in which it can be determined by the mixed color method after bringing the pH of the solution to 6. Bismuth does not interfere, even if present in amounts one hundred times as great as that of mercury. Silver likewise does not interfere. The authors effect the decomposition of the sample in a simple way by heating with a mixture of sulfuric and nitric acids in a flask provided with a condenser. Amounts of mercury ranging from 8  $\gamma$  (in one instance, 1  $\gamma$ ) to about 90  $\gamma$  added to 5 to 50 g. of vegetable and animal materials (blood, liver, urine, milk powder, cabbage,

<sup>9</sup> K. Müller, *Z. Physik*, **65**, 739 (1930); K. Müller and P. Pringsheim, *Naturwissenschaften*, **18**, 364 (1930); M. W. Zemansky, *Phys. Rev.*, **36**, 919 (1930).

<sup>10</sup> A. E. Ballard and C. D. W. Thornton, *Ind. Eng. Chem., Anal. Ed.*, **13**, 893 (1941).

<sup>11</sup> E. P. Laug and K. W. Nelson, *J. Assoc. Official Agr. Chem.*, **25**, 399 (1942).

etc.) were recovered satisfactorily (greatest variations were 92 and 106 per cent).

### Special Apparatus

A 500 ml. double-neck Pyrex distilling flask fitted with a Friedrichs extraction condenser and a 50 ml. dropping funnel (standard taper joints).

### Special Solutions

*Hydrochloric acid*, 0.25 *N*. Prepare from redistilled acid, and store in Pyrex.

*Hydroxylamine hydrochloride*, 20 per cent aqueous solution. To remove traces of metals reacting in acid solution, shake the solution with several portions of dithizone (0.01 per cent in chloroform), each one-tenth its volume.

*Potassium bromide*, 40 per cent (w/v) in water. Add a drop or two of 6 *N* sodium hydroxide to 1 liter of solution to make it slightly alkaline. Remove traces of heavy metals by shaking with dithizone until the last extract remains green. Any dithizone in the aqueous phase may be shaken out with chloroform after acidifying very slightly. Then make the solution very slightly basic with sodium hydroxide again, and store in a Pyrex bottle.

*Buffer solution*, 150 g. of  $\text{Na}_2\text{HPO}_4$  and 38 g. of anhydrous potassium carbonate in 1 liter of solution. Remove heavy metals by extraction with dithizone, and dithizone in the aqueous phase by extraction with large volumes of chloroform. Store in Pyrex.

*Dithizone*, 5.5 mg. per liter of redistilled U. S. P. chloroform. One per cent absolute alcohol may be added as a preservative.

### Procedure

Transfer 5 to 25 g. of sample (10–100  $\gamma$  Hg) to the digestion flask and add slowly through the dropping funnel 30 ml. or more of a 1:1 mixture of concentrated analytical reagent sulfuric and nitric acids. Heat gently, avoiding vigorous reaction and excessive foaming. With the full flame of the burner continue the digestion for 2 hours after most of the sample has been brought into solution. Add small amounts of nitric acid if charring occurs during the digestion. Fatty samples will contain large flakes of fatty acids at the end of the digestion. These may be filtered off without loss of mercury. Dilute the cold solution to a suitable volume and take a 1/10 aliquot for analysis.

Transfer the aliquot to a 250 ml. separatory funnel containing 50 ml. of 0.25 *N* hydrochloric acid, and then add 5 ml. of hydroxylamine hydrochloride solution and 10 ml. of dithizone. Shake vigorously for 1 minute, allow the phases to separate, and transfer the chloroform to a second separatory funnel containing 50 ml. of 0.25 *N* hydrochloric acid. Repeat the extraction with another 10 ml. portion of dithizone and add the chloroform to the second separatory funnel. Shake the latter for one-half minute to wash the chloroform solution.

Transfer the chloroform quantitatively to a third separatory funnel containing 50 ml. of 0.25 *N* hydrochloric acid and add 5 ml. of potassium

bromide solution. Shake vigorously for at least one-half minute to transfer the mercury to the aqueous phase. Draw off and discard the chloroform layer containing the copper dithizonate, and wash the aqueous solution with 5 or 10 ml. of chloroform. Draw off the chloroform as completely as possible. Add 10 ml. of buffer solution to raise the pH to *ca.* 6, followed by 10.0 ml. of dithizone solution, and shake for 1 minute. When the chloroform layer is free from suspended water droplets, run it into a suitable absorption cell, cover, and determine the transmittancy at 490 m $\mu$ . These final operations should be carried out in subdued light because of the light sensitivity of mercuric dithizonate (p. 93). A blank should be run.

### 2. The Method of Reith and van Dijk<sup>12</sup>

In brief, the method is as follows. The sample is decomposed with hydrochloric acid-potassium chlorate, excess chlorine is removed and mercury precipitated as the sulfide with copper sulfide as collector. The isolated mercury is brought into solution and a separation effected from most of the copper by regulated extraction of the former with dithizone from 1 *N* sulfuric acid. The dithizone extracts are shaken with a sulfuric acid solution of potassium permanganate to destroy the dithizonate and bring mercury into the aqueous phase. After removal of excess permanganate with hydroxylamine hydrochloride, the solution is tested for the possible presence of traces of oxidizing substances by shaking with a very small volume of dithizone, and if none is found, mercury is determined by the mixed color method (or extractive titration). If oxidizing substances are still present, mercury is re-extracted with dithizone, brought into aqueous solution with permanganate and then determined as mentioned.

Amounts of mercury ranging from 5 to 100  $\gamma$  showed 82 to 100 per cent recovery, mostly 90–95 per cent. No doubt the major part of the loss occurs in the decomposition of the sample. The authors state that small amounts (50  $\gamma$ ) of gold, palladium, platinum, and silver do not interfere in the determination.

#### Special Solutions

<sup>\*</sup> *Dithizone*, 0.001 per cent (w/v) in chloroform.

*Hydrochloric acid*. This may contain mercury and is purified as follows. Dilute the concentrated acid with an equal volume of water and add 1/10 its volume of concentrated sulfuric acid. Distil and collect the first 3/4 of the distillate.

*Hydroxylamine hydrochloride*. Dissolve 25 g. of the salt in 100 ml. of water, add 85 ml. of 4 *N* sodium hydroxide and shake the solution with small portions of a strong solution of dithizone in chloroform until the latter remains green. Then shake with chloroform until this remains colorless, and filter the solution. Add 120 ml. of 3 *N*

<sup>12</sup> J. F. Reith and C. P. van Dijk, *Chem. Weekblad*, **37**, 186 (1940).

sulfuric acid, filter off the precipitate, and dilute the filtrate to 500 ml. 1 ml. = 50 mg. hydroxylamine hydrochloride.

*Copper solution*, 1 ml. = 10 mg. Cu. 3.9 g. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 100 ml. of solution. If necessary the solution can be freed from mercury by adding a little sodium sulfide, allowing to stand for a few days and filtering.

### ¶ Procedure

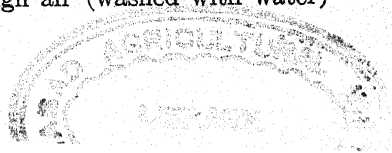
**Decomposition of Sample.**—In the case of urine, acidify with hydrochloric acid to bring any phosphate precipitate into solution and transfer a one-half liter sample to a 750 ml. Erlenmeyer flask. Add 4 g. of potassium chlorate and 180 ml. of hydrochloric acid, cover with a watch glass and heat on the water bath for  $1\frac{1}{2}$  hours. The liquid first turns brown, then light yellow. If necessary add 0.5 g. of potassium chlorate and heat for another  $1\frac{1}{2}$  hour period until the solution is light yellow.

In the case of organs, reduce the sample to fine state of subdivision by grinding and take a suitable weight, determined by the probable mercury content, for analysis. For example, transfer 30 g. of material to a 300 ml. Erlenmeyer flask, add 70 ml. of hydrochloric acid, 10 mg. of  $\text{Mn}^{++}$  (catalyst), and 1 g. of potassium chlorate. Cover and heat on a water bath. As soon as the liberated chlorine is consumed, add chlorate in 0.5–1 g. portions. The sample may be considered to be decomposed when the solution does not turn brown but remains light yellow for  $1\frac{1}{2}$  hours after the addition of the last portion of potassium chlorate. Make a note of the total amount of chlorate added so that the same quantity can be used in the blank.

Cool, filter through a plug of cotton previously washed with hydrochloric acid, and wash with hydrochloric acid and water (for example 25 + 25 ml. of hydrochloric acid and 125 + 100 ml. of water). The hydrochloric acid concentration of the filtrate should be about 5 per cent.

**Precipitation of Mercury with Hydrogen Sulfide.**—Add 5 ml. of hydroxylamine hydrochloride solution and 10 mg. of copper to the solution, and pass in hydrogen sulfide for 0.5–1 hour. Allow the flask to stand stoppered for 3 to 24 hours and then filter through a sintered glass filter (such as 11G4), keeping the precipitate in the flask so far as possible. Do not wash the precipitate, but blow air through the flask to drive out hydrogen sulfide. Add 10 ml. of chlorine water to the flask and the same volume to the filter, and pass chlorine into both. Allow to stand for one hour to assure decomposition of the sulfide precipitate; no black particles should be visible. Draw the solutions through the filter and catch the filtrate in a 200 ml. flask. Wash with water, keeping the volume of the filtrate and washings below 100 ml.

**Extraction of Mercury with Dithizone.**—Add 2.5 ml. of concentrated sulfuric acid to the solution and draw through air (washed with water)



for 15–20 minutes to remove most of the chlorine. To destroy the remaining chlorine add 5 ml. of hydroxylamine hydrochloride solution and allow to stand overnight (16 hours).

Transfer the solution to a separatory funnel and extract with *small* portions of dithizone, drawing off each portion into another separatory funnel. As long as mercury is present, an orange-colored chloroform layer is obtained. When practically all of the mercury has been extracted, the next portion of dithizone remains green for about one-half minute and then becomes brown (cuprous dithizonate) or violet (cupric dithizonate). Discontinue the extraction at this stage, and add the last extract to the rest.

**Destruction of Mercuric Dithizonate.**—Wash the combined extracts with 10 ml. of water (after shaking draw off the chloroform into another separatory funnel, leaving a few drops in the first funnel, then add a little chloroform to the latter, shake, and draw off into the second funnel). To the washed chloroform extract add 15 ml. of 1 *N* sulfuric acid and 0.5 ml. of 0.1 per cent potassium permanganate solution. Shake until the chloroform layer becomes nearly colorless (at most a pale yellow) and then 2–3 minutes more to be sure that all dithizonate has been decomposed. Decolorize the solution with hydroxylamine hydrochloride, add a few drops in excess and shake thoroughly to dissolve all manganese dioxide.

Draw off the chloroform into another separatory funnel and recover any mercury remaining in it by shaking for a few minutes with 10 ml. of 1 *N* sulfuric acid and 0.2 ml. of potassium permanganate. Add a few drops of hydroxylamine hydrochloride solution to clear the mixture, shake well, and combine the aqueous layer with the first aqueous solution.

Test the combined aqueous solutions for oxidizing agents by adding 0.3 ml. of 0.001 per cent dithizone solution and shaking well. If the chloroform becomes orange proceed with the colorimetric determination by the mixed color method as described in the next section. If it becomes yellow, an oxidizing agent is present and the mercury must be re-extracted as follows. Shake with 1 ml. portions of dithizone until 3 successive green extracts are obtained. Wash the combined extracts with a little water, and decompose the mercuric dithizonate as before with sulfuric acid and a few drops of potassium permanganate, decolorize with hydroxylamine hydrochloride, and finally test as before for the presence of oxidizing agents.

**Colorimetric Determination.**—Transfer the solution, together with the dithizone solution used in testing for oxidizing agents, to a 1.8 × 15 cm. glass-stoppered tube. Add small portions of dithizone with shaking after each addition until the color deviates slightly from the color of pure mercuric dithizonate solution. To an identical tube add the same amounts of sulfuric acid (preferably saturated with chloroform) and hydroxylamine

hydrochloride as present in the sample tube. Run in exactly the same volume of dithizone as present in the sample tube, and add standard mercuric chloride solution with thorough shaking until the hues of the chloroform layers match. To avoid error due to small amounts of copper present, it is advisable not to add any large excess of dithizone, since the larger the excess the greater the amount of copper going into the chloroform (p. 77).

Run a blank through the whole procedure.

### B. AIR

The determination of mercury vapor in air is best made by measuring the absorption of radiation of 253.7  $m\mu$  wave length. Special instruments for the purpose are available.<sup>13</sup> As little as 5  $\gamma$  of mercury per cubic meter of air can be detected. Less satisfactory are the chemical methods, of which the following is typical.

#### ¶ Procedure<sup>14</sup>

Pass the air, at a rate of 60–80 liters per hour, through two absorption tubes containing a mixture of 5 ml. of 0.1 *N* potassium permanganate and 5 ml. of 10 per cent sulfuric acid. After the absorption, make up the solution to volume and take an aliquot for analysis. Reduce the permanganate at room temperature with a slight excess of oxalic acid (or hydroxylamine hydrochloride, p. 328). Shake the solution with 0.5–1 ml. of 0.001 per cent dithizone in carbon tetrachloride or chloroform and compare against standards similarly obtained, or use the photometric method (p. 322).

<sup>13</sup> For descriptions and use see T. T. Woodson, *Rev. Sci. Instruments*, **10**, 308 (1939); V. F. Hanson, *Ind. Eng. Chem., Anal. Ed.*, **13**, 119 (1941); M. Shepherd, S. Schuhmann, R. H. Flinn, J. W. Hough, and P. A. Neal, *J. Research Natl. Bur. Standards*, **26**, 357 (1941).

<sup>14</sup> N. S. Kuzyatina, *Zavodskaya Lab.*, **8**, 174 (1939).

## CHAPTER XXIX

### MOLYBDENUM

The colorimetric determination of minute amounts of molybdenum in complex materials is easily carried out. There are a number of good methods available. Because of its great sensitivity and general freedom from interferences, the thiocyanate-stannous chloride method (IIA below) is usually superior to the others.

#### I. Separations

Special methods for the separation of molybdenum rarely need be applied when the thiocyanate-stannous chloride method with ether extraction is used, which in itself is a method of isolation. Many metals can be separated by precipitation with ammonium or sodium hydroxide, molybdenum (VI) being left in solution, but there are few data to show the extent of coprecipitation of molybdenum. A sodium carbonate fusion of a siliceous sample serves to bring molybdenum into solution without any significant retention by the residue.

Precipitation of molybdenum as the sulfide is a useful method of separation from metals not forming acid-insoluble sulfides. In the presence of tartaric acid a separation from tungsten can be effected in this way. Antimonic sulfide may be used as a collector.

Molybdenum cupferrate can be extracted with chloroform.<sup>1</sup> According to Park,<sup>2</sup> molybdenum can be quantitatively coprecipitated with manganese dioxide under the proper conditions, and a separation thus made from much copper.

For the separation of molybdenum from rhenium see p. 375.

#### II. Methods of Determination

##### A. THE THIOCYANATE-STANNOUS CHLORIDE METHOD

In acid solution in the presence of a suitable reducing agent such as stannous chloride, thiocyanate gives an amber to orange-red color with molybdenum. The colored compound is a thiocyanate complex of quinquevalent molybdenum,<sup>3</sup> which can be extracted by such solvents as ethyl ether, butyl acetate, or cyclohexanol.

<sup>1</sup> D. Bertrand, *Bull. soc. chim.*, **6**, 1676 (1939).

<sup>2</sup> B. Park, *Ind. Eng. Chem., Anal. Ed.*, **6**, 189 (1934).

<sup>3</sup> C. F. Hiskey and V. W. Meloche, *J. Am. Chem. Soc.*, **62**, 1565 (1940). According to these authors the ratio CNS/Mo in the colored complex is 3.



The color intensity given by a constant quantity of molybdenum depends upon a number of factors such as the acidity, the concentration of thiocyanate, and the time of standing. The effect of these variables has been studied by Hurd and Allen.<sup>4</sup> They found that the acidity of the solution in hydrochloric acid should be 5 per cent. At this acidity the color intensity remains very nearly constant for an hour, after showing a slight decrease for the first 5 minutes after mixing the reagents (1 per cent potassium thiocyanate present). Acidities higher and lower than this give less color and greater fading. Fading is especially marked in strongly

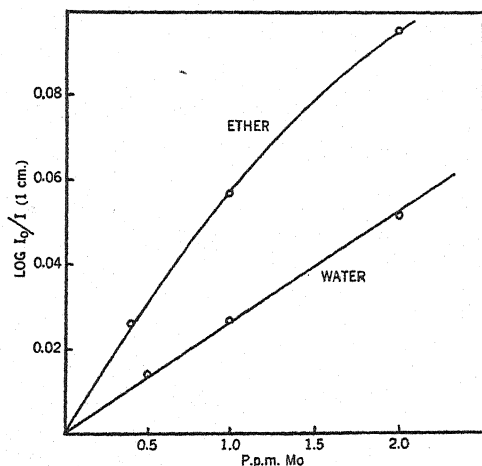


Fig. 45.—Determination of molybdenum by the thiocyanate-stannous chloride method according to directions on p. 333 (blue filter). An aqueous molybdenum thiocyanate solution containing 1.00 p.p.m. of Mo gave the same reading 2 minutes and 30 minutes after addition of reagents; a 2.00 p.p.m. solution showed 1.90 p.p.m. after 30 minutes. An ether solution containing 2.00 p.p.m. of Mo showed 2.12 p.p.m. after standing for 90 minutes.

acid solutions. The potassium thiocyanate concentration should be 0.6 per cent or greater; below this concentration, fading is marked. The concentration of stannous chloride plays a minor role; 0.04 and 0.8 per cent concentrations give practically the same results. Stannic chloride (formed when ferric iron is present in the sample) shows a slight tendency to cause fading of the color.

In various organic solvents the thiocyanate complex is more stable than in aqueous solution. In ethyl ether (or a 2:1 mixture of ethyl ether and petroleum ether) which has been shaken with thiocyanate and stannous chloride, the color intensity remains practically constant or shows a

<sup>4</sup> L. C. Hurd and H. O. Allen, *Ind. Eng. Chem., Anal. Ed.*, 7, 396 (1935).

slight decrease over a period of an hour and then increases very gradually. Cyclohexanol, previously saturated with the reagents, gives a solution that shows practically no change in color intensity for a few hours, but on long standing exhibits a slow increase. Butyl acetate solutions of the complex become darker fairly rapidly on standing, especially if the solvent has first been shaken with a mixture of thiocyanate, stannous chloride, and acid, according to the authors mentioned. Grimaldi and Wells<sup>5</sup> recommend developing the molybdenum-thiocyanate color in a water-acetone solution, because the "acetone appears to have a stabilizing action and prevents fluctuations of the color with time."

If ether or other organic solvent is used to extract the molybdenum thiocyanate, the determination can be made the presence of most elements. Among the metals that do not interfere are iron, aluminum, titanium,

TABLE 46  
DETERMINATION OF MOLYBDENUM IN ROCKS BY THE THIOCYANATE-STANNOUS CHLORIDE METHOD

Sample	MoO <sub>3</sub> present %	MoO <sub>3</sub> found %
Granite (0.1 g.) + 10% P <sub>2</sub> O <sub>5</sub> .....	0.007	0.008
Granite (0.1 g.) + 0.5% F.....	0.007	0.007
Diorite (0.5 g.).....	0.0003	0.00035
Diorite (0.5 g.).....	0.0003	0.00025
Synthetic acid rock (0.5 g.).....	0.0007	0.00075
Synthetic acid rock (0.5 g.) + 0.05% WO <sub>3</sub> .....	0.0007	0.0009

manganese, nickel, cobalt, uranium, and tantalum. Chromium is practically without effect, but in high concentrations may impart a very faint greenish coloration to the ether. Vanadium in relatively high concentrations colors the ether slightly. Phosphate in reasonable amounts is without effect (Table 46). Much fluoride leads to low results but moderate amounts (100 F: 1 Mo) do not interfere. Tungsten alters the hue of the ether solution (greenish-yellow), but the effect of small amounts (50 W/ 1 Mo) is not serious. Tartrate or citrate prevents the interference of tungsten, both in the ether extraction and in the non-extraction method (see p. 336).

Platinum is reduced by stannous chloride to chloroplatinous acid which is extracted by ether (yellow-brown color). Such quantities of platinum as may be introduced from a sodium carbonate fusion in a platinum crucible are too small to have any significant effect. Rhodium also colors the ether layer. Gold, tellurium, and selenium are reduced by stannous

<sup>5</sup> F. S. Grimaldi and R. C. Wells, *Ind. Eng. Chem., Anal. Ed.*, **15**, 315 (1943).

chloride to the elements but small amounts should not interfere. Copper in more than small amounts gives a precipitate of cuprous thiocyanate.

Rhenium reacts in practically the same way as molybdenum, but its effect rarely has to be considered.<sup>6</sup>

The transmittancy curve of molybdenum thiocyanate in ether is similar to that of rhenium thiocyanate (Fig. 55, p. 377), with a minimum at *ca.* 475  $m\mu$ .

### Special Solutions

*Potassium thiocyanate*, 5 per cent.

*Stannous chloride*, 10 g.  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 ml. of 2 *N* hydrochloric acid. The tin is oxidized on standing and the solution should therefore be prepared fresh relatively frequently.

*Ethyl ether*. Shake reagent-quality ether with 1/10 its volume of equal amounts of stannous chloride and potassium thiocyanate solutions the same day it is to be used.

*Standard molybdenum solution*, 0.01 per cent Mo. Dissolve 0.075 g. of pure  $\text{MoO}_3$  in a few milliliters of dilute sodium hydroxide solution, dilute with water, make slightly acid with hydrochloric acid and make up to 500 ml. with water. An aliquot of this solution may be diluted to 0.001 per cent molybdenum if desired.

### ¶ Procedure

**Without Ether Extraction.**<sup>7</sup>—Acidify the sample solution, having a volume in the neighborhood of 25 ml. and containing up to 200  $\gamma$  of molybdenum, with 5 ml. of concentrated hydrochloric acid. Add 6–7 ml. of potassium thiocyanate solution, mix, then add 2 ml. (or more if iron or other reducible substances are present) of stannous chloride, and dilute with water to 50 ml. in a volumetric flask. Determine the transmittancy of the solution within 15 minutes, preferably less, using a blue filter (maximum transmission at about 475  $m\mu$ ). Prepare the standards in the same way as the sample; if the sample solution contains iron, the same approximate amount should preferably be added to the standards.

**Ether Extraction.**—The extraction procedure should be applied when the greatest sensitivity is required or colored substances are present in the sample solution.

For amounts of molybdenum in the vicinity of 25–50  $\gamma$ , add 4 ml. of hydrochloric acid to the solution and dilute with water to 45–50 ml.<sup>8</sup> in

<sup>6</sup> For the determination of molybdenum in the presence of much rhenium consult J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **23**, 497 (1939).

<sup>7</sup> When much tungsten is present, follow the procedure on p. 336.

<sup>8</sup> The level of the liquid is preferably marked on the funnel with a strip of gummed paper or a wax-pencil mark so that the standards for the calibration curve can be diluted to the same approximate volume. In this way errors due to the small amount of unextracted molybdenum will be eliminated. If the volume of the aqueous solution can be kept below 50 ml. this should be done, and the amount of acid and thiocyanate reduced accordingly.

a separatory funnel. Cool the solution to 15°C., add 6 to 7 ml. of potassium thiocyanate solution, mix, and add 2 ml. (or more as required) of stannous chloride. Shake the solution to mix well and after 1 minute add 15 ml. of ether. Shake, with the usual precautions, for  $\frac{1}{4}$ – $\frac{1}{2}$  minute and allow the two liquids to separate. Draw off the water layer into a beaker, dry the stem of the funnel with a rolled-up filter paper, and deliver the ether into a dry 25 ml. volumetric flask. Return the aqueous solution to the separatory funnel and extract with a 10 ml. portion of ether. Combine this extract with the first and dilute to 25 ml. with ether. Transfer the mixed solution to a suitable cell, cover, and determine the transmittancy with the aid of a blue filter. A filter giving maximum transmittancy in the range 450–500  $m\mu$  is suitable. Wratten filters 45 or 47A are satisfactory. Prepare the standard extracts in the same manner as the extract of the sample.

When very small amounts of molybdenum (1–2  $\gamma$ ) are to be determined, the standard series method or colorimetric titration may be applied to advantage. See p. 335.

## B. OTHER METHODS

In hot mineral acid solution, phenylhydrazine gives a red-colored product with molybdate.<sup>9</sup> The color is stable. The sensitivity of the reaction is fairly high. Tungsten gives no color, vanadium a green color. The reaction has been applied in the determination of molybdenum in silicate rocks<sup>10</sup> and in manganese ores.<sup>11</sup>

Potassium ethyl xanthate  $\text{SC} \begin{array}{l} \text{SK} \\ \text{OC}_2\text{H}_5 \end{array}$  reacts with molybdenum in

faintly acid solution to give a red-colored compound<sup>12</sup> which may be extracted with chloroform.<sup>13</sup> Various heavy metals (copper, iron, etc.) also give colored products with xanthate.

Other reagents that have been used for the colorimetric determination of molybdenum include hydrogen sulfide<sup>14</sup> (colloidal  $\text{MoS}_3$  formed), tannic

<sup>9</sup> L. Spiegel and T. Maas, *Ber.*, **36**, 512 (1903); E. Montignie, *Bull. soc. chim.*, [4], **47**, 128 (1930). It is stated that phenylhydrazine is oxidized by molybdate to diazonium salt which couples with the excess phenylhydrazine and molybdate.

<sup>10</sup> G. von Hevesy and R. Hobbie, *Z. anorg. allgem. Chem.*, **212**, 134 (1933).

<sup>11</sup> H. Hauptmann and M. Balconi, *Z. anorg. allgem. Chem.*, **214**, 380 (1933).

<sup>12</sup> Perhaps  $\text{MoO}_3 \cdot [\text{SC}(\text{SX})(\text{OC}_2\text{H}_5)]_2$  according to Feigl.

<sup>13</sup> S. L. Malowan, *Z. anorg. allgem. Chem.*, **103**, 73 (1919); *Z. anal. Chem.*, **79**, 202 (1929).

<sup>14</sup> E. Wendehorst, *Z. anorg. allgem. Chem.*, **144**, 319 (1925); J. M. McCandless and J. I. Burton, *Ind. Eng. Chem.*, **19**, 406 (1927); H. ter Meulen, *Rec. trav. chim.*, **51**, 549 (1932); D. Bertrand, *Bull. soc. chim.*, **6**, 1676 (1939).

acid,<sup>15</sup> hydrogen peroxide,<sup>16</sup> and sodium thiosulfate<sup>17</sup> (lilac-colored reduction product in acid solution, extractable with ether or ethyl acetate).

### III. Special Applications of the Thiocyanate-Stannous Chloride Method

#### A. SILICATE ROCKS

The following procedure permits the determination of quantities of molybdenum as small as 0.0001 per cent.

##### ¶ Procedure<sup>18</sup>

Fuse 1 g. of rock powder with sodium carbonate and leach the melt as described on p. 196. Transfer 50 ml. of the filtrate which has been made up to 100 ml. to a separatory funnel and add slowly, while swirling, 8 ml. of concentrated hydrochloric acid. Shake the solution carefully to liberate carbon dioxide in supersaturated solution and cool to 15–20°. Add 3 ml. of 5 per cent potassium thiocyanate solution, mix, and then add 3 ml. of 10 per cent stannous chloride solution in 2 *N* hydrochloric acid. Mix and allow to stand for  $\frac{1}{2}$ – $\frac{3}{4}$  minute. Add 6 to 7 ml. of ether which has been shaken with thiocyanate and stannous chloride (p. 333), shake well for  $\frac{1}{2}$  minute, allow the two liquids to separate, draw off the aqueous layer into a beaker, and run the ether into a color comparison tube having a diameter of 10 mm. and preferably provided with a glass stopper (p. 42). Return the aqueous solution to the separatory funnel, extract with 2 to 3 ml. of ether, and combine the latter with the first extract. Usually two extractions will suffice, but as a precaution extract once more with 2 ml. of ether and add this extract to the others if it shows any significant amount of color.

Compare the combined ether extract against a series of standards which have been obtained by extracting known molybdenum solutions having about the same volume and composition as the sample. Alternatively use the colorimetric titration technique as follows. Prepare a standard solution of molybdenum thiocyanate in ether by adding to 50 ml. of aqueous solution containing 0.25 mg. of molybdenum and 2.5 g. of sodium carbonate, 8 ml. of concentrated hydrochloric acid, 3 ml. of potassium thiocyanate, and 3 ml. of stannous chloride, and extracting the cold mixture with 10, 5, 5, 5 and 5 ml. portions of ether (the last extract should be colorless or very nearly so). Deliver the extracts into a 25 ml. volumetric flask and make up to the mark with ether. Using gentle suction draw the ether solution into a dry microburet, which has been cooled to 15–20° if neces-

<sup>15</sup> O. Steiner, *Z. anal. Chem.*, **81**, 389 (1930).

<sup>16</sup> A. D. Funck, *Z. anal. Chem.*, **68**, 283 (1926).

<sup>17</sup> P. Falcicola, *Ann. chim. applicata*, **17**, 261 (1927).

<sup>18</sup> E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 336 (1936).

sary, and cover well. Add the ether solution to a color comparison tube containing approximately the same volume of ether as the sample tube until the colors match when the tubes are viewed axially. The standard ethereal molybdenum thiocyanate solution must be prepared fresh each 3-4 hours because its color intensity slowly increases on standing. In all the operations care must be taken to prevent any significant evaporation of ether from the standard solution. The room temperature should be 20° or less if possible.

Run a blank through the whole procedure.

### B. TUNGSTEN ORES

Grimaldi and Wells (*loc. cit.*) have described a procedure for the determination of small amounts of molybdenum in tungsten and molybdenum ores. The thiocyanate color is developed in water-acetone solution and citrate is used to prevent the interference of tungsten. Iron is stated to interfere in the method by giving a slight color and it must be removed. When tungsten is present, phosphorus in more than small amounts (about 30 mg.) interferes by causing the molybdenum color to fade and slowly giving a blue color. Large quantities of vanadium impart a blue-green color. A few hundredths of a milligram of molybdenum can be accurately determined in the presence of 0.2 g. or more of tungstic oxide.

### ¶ Procedure

The following directions are those of Grimaldi and Wells. The colorimetric titration technique is applied in the color comparison, but of course the photometric method can be applied to advantage, especially when very small amounts of molybdenum are involved.

With substances such as scheelite containing up to 40 per cent of tungstic oxide and as much as 1 per cent of molybdenum oxide, fuse a 0.5 g. sample with 2.5 g. of sodium carbonate and, if thought necessary, 0.05 g. of sodium nitrate. Extract the melt with water containing a drop or two of alcohol to reduce manganate, filter, and wash with 1 per cent sodium carbonate solution. Make the filtrate just acid with hydrochloric acid. If any chromate is present, reduce it with sulfurous acid. Evaporate the solution to a volume of about 25 ml. to remove carbon dioxide. Disregard any silica that may separate. Neutralize with 10 per cent sodium hydroxide and add an excess of 10 ml., digest on the steam bath for ten minutes, filter hot, and wash with dilute sodium hydroxide. Make the filtrate barely acid with hydrochloric acid (phenolphthalein as indicator) and dilute to exactly 100 ml. (Molybdenite and wulfenite ores are best brought into solution by acid treatment according to the usual procedures.)

Transfer a 15 ml. aliquot of the sample solution to a 100 ml. beaker and add 1.5 g. of ammonium citrate. When the latter has dissolved add 5 ml. of 10 per cent ammonium thiocyanate and 25 ml. of acetone, cool, and add dropwise exactly 7 ml. of 10 per cent stannous chloride in 1:1 hydrochloric acid. In another 100 ml. beaker prepare a similar blank solution and add to it standard molybdenum solution (1 ml.  $\equiv$  0.1 mg.  $\text{MoO}_3$ ) until the color matches that of the sample solution.

#### C. STEEL

##### ¶ Procedure<sup>19</sup>

Dissolve 0.2 g. (for less than 0.2 per cent Mo) of sample in 10 ml. of 1:4 sulfuric acid, warming to hasten solution. When action has ceased, add 1 ml. of 30 per cent hydrogen peroxide and boil for 5 minutes. If any insoluble material remains filter it off on paper and wash with water. Boil the solution down to 5 ml. to destroy excess hydrogen peroxide. If tungstic acid has separated add 0.5 g. of tartaric or citric acid followed by sodium hydroxide solution (2 to 4 *N*) until the solution is slightly basic. Then add 15 ml. of 1:4 sulfuric acid, transfer to a separatory funnel and dilute to 40–50 ml. with water. Cool the solution if necessary and add 5 ml. of potassium thiocyanate solution (5 per cent). Mix and add 5 ml. of stannous chloride solution (300 g.  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 1 liter 1:9 hydrochloric acid). Cool the solution to room temperature under the tap, add 30 ml. of ether (previously shaken with stannous chloride and thiocyanate, p. 333) and shake well for 1/2 minute. Allow the layers to separate, draw off the aqueous solution and transfer the ether layer, without any appreciable amount of aqueous phase, to a 50 or 100 ml. volumetric flask. Extract the aqueous phase with a 20 ml. portion of ether, combine the latter with the first portion, and make up to 50 or 100 ml. with ether. Transfer the mixed solution to the cell of a photometer, cover, and determine the extinction (p. 334).

Construct the reference curve by extracting with ether ferric sulfate solutions which contain the equivalent of 0.2 g. of iron and various amounts of molybdenum, and which have been treated in the same manner as the sample solution.

#### D. BIOLOGICAL MATERIALS

The following procedure for the determination of molybdenum in plant materials<sup>20</sup> may be regarded as a typical one for this class of materials.

<sup>19</sup> Essentially the directions given by T. R. Cunningham and H. L. Hamner, *Ind. Eng. Chem., Anal. Ed.*, **13**, 106 (1941).

<sup>20</sup> F. B. Marmoy, *J. Soc. Chem. Ind.*, **58**, 275 (1939); K. E. Stanfield, *Ind. Eng. Chem., Anal. Ed.*, **7**, 273 (1935).

### ¶ Procedure

Ash 2 g. of sample in a silica dish in a muffle furnace at 450–500°. Moisten the ash with water, add 10 ml. of concentrated hydrochloric acid, transfer to a small beaker, dilute to about 40 ml. with water, and boil for 5 minutes. Filter the solution through paper into a 100 ml. volumetric flask and wash with water. If the amount of the insoluble material is appreciable, ignite the paper, and fuse the residue with sodium carbonate. Extract the melt with water, filter, and add the filtrate and washings to the volumetric flask. Dilute to 100 ml., transfer an aliquot, usually 50 ml., containing 1 to 20  $\gamma$  of molybdenum to a separatory funnel and determine molybdenum according to the directions on p. 333.

Organic matter may also be destroyed by wet oxidation (see, for example, p. 278).



## CHAPTER XXX

### NICKEL

#### I. Separations

The solubility of nickel (II) dimethylglyoxime in chloroform<sup>1</sup> (pale yellow solution) provides an easy means of separation of minute amounts of nickel in the analysis of silicate rocks, biological material, water, etc.<sup>2</sup> From a faintly ammoniacal solution containing citrate, nickel may thus be separated by extraction from ferric iron, aluminum, cobalt, etc. Copper accompanies nickel to a greater or less extent in the extraction, but much of the copper is removed from the chloroform extract when it is shaken with dilute ammonia, whereas nickel remains in the chloroform. The cobalt compound of dimethylglyoxime (brown) is not extracted by chloroform to any significant extent since the latter remains colorless, but much cobalt naturally interferes by consuming the reagent. Nevertheless a satisfactory separation of nickel from a thousand times as much cobalt can be effected (see Table 48).<sup>3</sup>

Much manganese interferes in the extraction of nickel, probably by oxidizing the latter to the nickelic condition in the ammoniacal solution; nickelic dimethylglyoxime is not extracted by chloroform. This interference can be prevented by adding hydroxylamine hydrochloride to keep manganese in the divalent state.

The nickel dimethylglyoxime in the chloroform may be decomposed and nickel transferred to the aqueous phase by shaking with dilute hydrochloric acid; most of the dimethylglyoxime remains in the chloroform. The nickel in the acid solution may then be determined most conveniently by the dimethylglyoxime method (IIA).

#### II. Methods of Determination

##### A. THE DIMETHYLGLYOXIME METHOD

A very satisfactory method for the determination of small quantities of nickel is based on the wine-red or brown color obtained when dimethylglyoxime is added to a basic solution of a nickel salt which has been treated

<sup>1</sup> The solubility of nickel dimethylglyoxime in chloroform at room temperature corresponds to approximately 0.05 mg. of nickel per milliliter.

<sup>2</sup> E. B. Sandell and R. W. Perlich, *Ind. Eng. Chem., Anal. Ed.*, **11**, 309 (1939).

<sup>3</sup> At more unfavorable ratios cobalt may presumably be precipitated as potassium cobaltinitrite or  $\alpha$ -nitroso- $\beta$  naphtholate, but no data are available.

with an oxidizing agent such as bromine.<sup>4</sup> The colored compound formed in the reaction is nickelic (IV) dimethylglyoxime. The sensitivity of the reaction is great, being approximately equal to that of the iron-thiocyanate reaction.

The hue and color intensity of the nickelic dimethylglyoxime solution depend upon the original acidity of the nickel solution. If bromine water is added to an acid solution followed by ammonia and glyoxime, a brownish solution is obtained, while if bromine is added to a faintly ammoniacal or neutral solution (followed by ammonia in the latter case) a wine-red

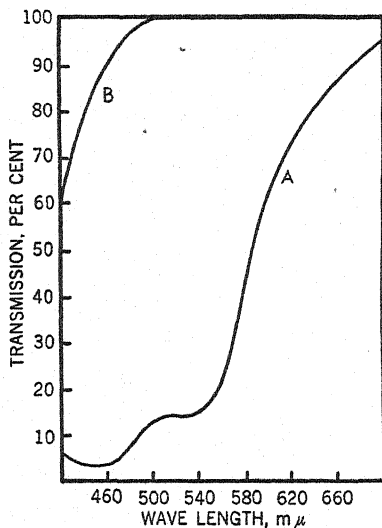


Fig. 46.—Transmission curves of (A) nickelic dimethylglyoxime solution (5 minutes after preparation) and (B) ammoniacal solution of ferric iron-containing citrate. (From Murray and Ashley, *Ind. Eng. Chem., Anal. Ed.*, **10**, 1 (1938).)

color is produced. The color intensity is stronger in solutions initially ammoniacal or neutral (*cf.* Table 47). A variation in the acidity of the sample solution from 0.25 to 0.5 *N* (hydrochloric acid) has no effect on the color intensity.

The procedure given below calls for an initially acid solution of the sample, such as is usually encountered in practice. Under constant conditions highly reproducible values are obtained. The full color intensity develops nearly immediately after the addition of the glyoxime and undergoes hardly any change in a quarter of an hour, but increases slowly on long standing, and finally fades slowly. Thus under the conditions de-

<sup>4</sup> This reaction was discovered by F. Feigl, *Ber.*, **57**, 758 (1924), and applied quantitatively by A. Rollet, *Compt. rend.*, **183**, 212 (1926).

scribed on p. 343, a solution containing 10.0  $\gamma$  of nickel in 25 ml. showed an apparent content of 10.0  $\gamma$  20 minutes after mixing, 10.5  $\gamma$  after 1 hour, 10.9  $\gamma$  after 2.5 hours and 7.4  $\gamma$  after 23 hours; a solution containing 5.0  $\gamma$

TABLE 47

DETERMINATION OF NICKEL WITH DIMETHYLGLYOXIME (EFFECT OF VARIATIONS IN PROCEDURE AND OF SOME FOREIGN METALS)

Except as indicated, 10.0  $\gamma$  Ni in 10 ml. 0.5 *N* hydrochloric acid, 0.3 ml. bromine water, 2-3 drops ammonia in excess, 0.5 ml. 1% dimethylglyoxime; final volume 25 ml. Green filter.

Variation in procedure	Ni found $\gamma$
Neutral nickel solutions.....	13.1
10 ml. 0.25 <i>N</i> HCl.....	10.0
1.0 ml. bromine water.....	9.3
0.50 g. NaCl.....	10.0
0.50 g. sodium citrate.....	Weak color
0.50 g. sodium citrate, 1 ml. bromine water.....	9.1
1.0 mg. Fe <sup>III</sup> , 0.50 g. sodium citrate, 1 ml. bromine water (compared against similar standard).....	11.5
0.2 mg. Cu.....	15.3
0.2 mg. Co.....	11.7

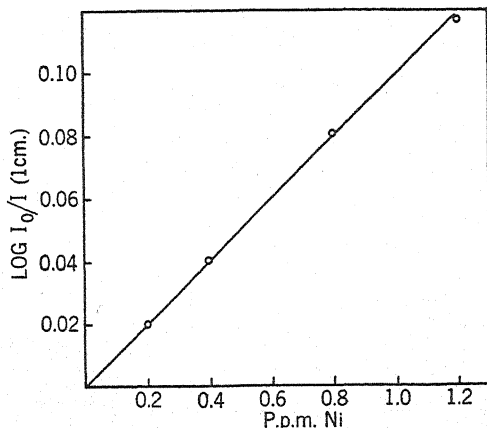


Fig. 47.—Determination of nickel by the dimethylglyoxime method according to the directions in the text (green filter).

of nickel gave 5.5  $\gamma$  after 1.5 hours. Beer's law is followed (Fig. 47) up to 5 p.p.m. of nickel under the conditions of the procedure given below.

Copper and cobalt also give colors with dimethylglyoxime but these are so much weaker than the nickel color that these metals do not interfere

if their amount is equal to or less than that of nickel. Citrate or tartrate may be added to prevent the precipitation of iron, aluminum, etc. The light yellow solution of ferric iron in alkaline citrate absorbs very slightly above 500  $m\mu$ . Nickelic dimethylglyoxime solution on the other hand absorbs strongly in the neighborhood of 540  $m\mu$  (Fig. 46), so that by the use of a suitable filter nickel may be determined in the presence of iron. If a sufficiently selective filter is not available, nickel may be separated from iron by the simple method described below.

### Special Solutions

*Dimethylglyoxime solution*, 1 per cent in ethyl alcohol. The solution is stable.

*Sodium citrate*, 10 per cent in water.

*Bromine water*, saturated.

*Chloroform*, reagent quality.

TABLE 48

DETERMINATION OF NICKEL WITH DIMETHYLGLYOXIME AFTER SEPARATION BY CHLOROFORM EXTRACTION OF THE DIMETHYLGLYOXIME COMPOUND

Foreign metals	Ni taken $\gamma$	Ni found $\gamma$
17.5 mg. Fe <sup>III</sup> .....	5.0	4.8
		4.5
17.5 mg. Fe <sup>III</sup> , 0.08 mg. Cu.....	2.5	2.5
17.5 mg. Fe <sup>III</sup> , 0.25 mg. Cu, 0.13 mg. Co.....	2.5	2.7
17.5 mg. Fe <sup>III</sup> , 2.5 mg. Mn <sup>II</sup> .....	2.5	2.5
17.5 mg. Fe, 0.5 mg. Cr <sup>VI</sup> , 0.13 mg. V <sup>V</sup> .....	5.0	5.0
5 mg. Co <sup>a</sup> .....	5.0	4.5

<sup>a</sup> 3.5 ml. 1% dimethylglyoxime used in chloroform extraction.

*Standard nickel solution*, 0.00100 per cent in 0.1 *N* hydrochloric acid. It may be prepared from uneffloresced crystals of nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}/\text{Ni} = 4.05$ ) or from pure nickel metal.

### Procedure

**Extraction of Nickel.**—To 5–20 ml. of slightly acid solution, preferably containing 5  $\gamma$  or more nickel, add 5 ml.<sup>5</sup> of sodium citrate and make slightly ammoniacal (a few drops of concentrated ammonia in excess). Add 2 ml. (or more if much cobalt is present) of dimethylglyoxime solution and extract in a small separatory funnel with three 2 to 3 ml. portions of chloroform, shaking for one-half minute each time. Shake the combined chloroform extracts with 5 ml. of 1:50 ammonia, and run the chloroform into another separatory funnel; shake the water layer with a milliliter or two of chloroform and combine the latter with the washed extract.

<sup>5</sup> Or enough to keep iron (III), aluminum, etc. from precipitating.

Shake the chloroform solution vigorously for 1 minute with two portions of 0.5 *N* hydrochloric acid, each having a volume of 5 ml. (or slightly less if the solution is finally made up to 10 ml.). Transfer the hydrochloric acid solutions to a volumetric flask of suitable size (*cf.* Fig. 47), or to a color comparison tube if the standard series method is to be used. If a Duboseq colorimeter is to be used the nickel concentration should be greater than 1  $\gamma$  per ml. Not more than 6  $\gamma$  nickel should be present in 1 ml. of solution because above this concentration a precipitate may form.

**Colorimetric Determination.**—Add 5 drops of bromine water to the acid sample solution or an aliquot of it, and then concentrated ammonium hydroxide until the color of bromine is destroyed,<sup>6</sup> followed by an excess of 3–4 drops. Finally add 0.5 ml. of dimethylglyoxime solution and dilute to volume with water. Use a green filter (maximum transmission at 520–530  $m\mu$ ) in determining the transmittancy. The standard nickel solutions for the construction of the reference curve should have approximately the same original acidity as the sample solution. The color intensity increases slowly with time so that readings should be made within 5 minutes after mixing. Run a reagent blank.

## B. OTHER METHODS

Potassium dithiooxalate imparts a deep red coloration to neutral or slightly acid nickel solutions.<sup>7</sup> The reaction is highly sensitive and Beer's law is followed, but unfortunately the majority of the cations interfere by giving more or less strong colors. Among the noninterfering ions may be mentioned the alkali and alkaline earth metals, aluminum, phosphate and manganese, the latter in amounts less than 300 p.p.m. Both iron and cobalt give strong colors.

Potassium dithiocarbonate produces a red to brown color in ammoniacal nickel solution.<sup>8</sup> This reagent is inferior to potassium dithiooxalate.

Formaldoxime has also been used as a nickel reagent but has little to recommend it for general purposes.<sup>9</sup>

## III. Applications of the Dimethylglyoxime Method

### A. SILICATE ROCKS

#### ¶ Procedure

Weight 0.25 gram of finely powdered basic rock (0.01 to 0.05 per cent nickel), or 0.5 gram or more of acidic rock, into a platinum dish, add a few milliliters of water, 0.5 ml. of 70 per cent perchloric acid, and 2.5 ml. of

<sup>6</sup> Sometimes the solution does not become entirely colorless because enough dimethylglyoxime may be present to give a visible reaction with the nickel.

<sup>7</sup> J. H. Yoe and F. H. Wirsing, *J. Am. Chem. Soc.*, **54**, 1866 (1932).

<sup>8</sup> I. V. Lindt, *Z. anal. Chem.*, **53**, 165 (1914).

<sup>9</sup> G. Denigès, *Bull. soc. pharm. Bordeaux*, **70**, 101 (1932).

hydrofluoric acid (for a sample greater than 0.25 gram these amounts should be correspondingly increased). Evaporate the mixture to dryness, take up the residue in 0.5 ml. of perchloric acid and 2 or 3 ml. of water, and again evaporate to dryness. To the residue add 0.5 to 1 ml. of concentrated hydrochloric acid and 5 ml. of water. Heat to bring all soluble material into solution, add 5 ml. of 10 per cent sodium citrate solution, neutralize the cold solution with concentrated ammonium hydroxide using litmus paper, and add a few drops in excess. If there is an appreciable amount of precipitate or residue in the solution at this point, filter through a small paper, wash with small portions of water, and ignite the paper and its contents. Fuse the residue with approximately 0.1 gram of sodium carbonate, add an excess of dilute hydrochloric acid to the cooled melt, and heat to effect as complete solution as possible. Add 2 or 3 ml. of 10 per cent sodium citrate solution, make slightly ammoniacal, and reserve the solution.

To the main solution (filtrate from any insoluble material) add 2 ml. of 1 per cent alcoholic dimethylglyoxime solution, and shake vigorously for one-half minute with two or three portions of reagent-quality chloroform, each having a volume of 2 or 3 ml. In a similar manner extract the ammoniacal solution of the sodium carbonate melt. Combine all the chloroform extracts and shake vigorously with 5 ml. of 1 to 50 ammonium hydroxide solution. Draw off the chloroform, taking care that no drops of the aqueous phase accompany it, and shake the water layer with a milliliter or two of chloroform to recover any suspended drops of chloroform solution. Then proceed as described on p. 343.\*

#### B. STEEL

It has not been ascertained whether small amounts of nickel can be determined accurately in steel by extracting nickel dimethylglyoxime from the solution of the sample with chloroform and then following the general procedure above. The following method, due to Murray and Ashley,<sup>10</sup> has been used for determining relatively much nickel (more than 0.5 per cent) in steel, but it should be applicable to amounts as low as 0.1 per cent, and perhaps less if the amount of sample represented by the aliquot taken is increased. In this procedure, iron is not removed, and the nickelic dimethylglyoxime is formed in an ammoniacal citrate solution. As already mentioned, ferric iron in such a solution shows practically no absorption above 500 m $\mu$ , and does not interfere if light of suitable wave length, or a proper filter, is used in the measurement of the transmittancy. A slight absorption of light by iron would be immaterial as long as the sample solution contained the same concentration of iron as the standard solutions

<sup>10</sup> W. M. Murray and S. E. Q. Ashley, *Ind. Eng. Chem., Anal. Ed.*, **10**, 1 (1938).

used in the construction of the standard curve. This condition can frequently be fulfilled quite closely. Copper will interfere if it exceeds nickel in amount (see Table 47). There are no data available to indicate the effect of manganese when it greatly predominates over nickel.

#### ¶ Procedure<sup>11</sup>

Dissolve 0.50 g. of steel in 10 ml. of warm 1:1 nitric acid. Boil to expel oxides of nitrogen, cool, and dilute to 250 ml. with water. Mix, allow any insoluble material to settle to the bottom and transfer 5 ml. of the solution to a 50 ml. volumetric flask. Add in succession, with mixing after each addition, 5 ml. of 10 per cent citric acid solution, 2 ml. of saturated bromine water, 2 ml. of 1:1 ammonium hydroxide, and 1 ml. of 1 per cent alcoholic dimethylglyoxime solution. Dilute to the mark with water, mix, and determine the transmittancy of the solution within 10 minutes, using a green filter with mean transmission at 530 m $\mu$ . The known nickel solutions for the standard curve should contain the same concentration of nickel-free iron as the sample solution.

### C. BIOLOGICAL MATERIALS

The quantity of sample taken should preferably be such that 5  $\gamma$  or more of nickel are present. The organic material is destroyed by acid digestion (see p. 278) or by ignition. The latter procedure will be satisfactory if the ash can be brought completely into solution with hydrochloric acid (*cf.* p. 14), but the digestion method is perhaps to be preferred. If copper should be present in relatively large amounts ( $\text{Cu}:\text{Ni} > 100$ ) it should be removed by reducing the acidity to 0.1–0.2 *N* and extracting the solution with only a slight excess of a 0.01 per cent solution of dithizone in carbon tetrachloride or chloroform (see p. 215); droplets of dithizone remaining should be completely removed by shaking the aqueous layer with small portions of carbon tetrachloride or chloroform. Alternatively copper can be removed by hydrogen sulfide precipitation. The excess hydrogen sulfide must be completely removed from the filtrate by boiling. The acid solution is then treated with sodium citrate and excess ammonia, dimethylglyoxime is added, the nickel compound of the latter is extracted with chloroform as described on p. 342 and nickel finally determined according to the general procedure on p. 343.

<sup>11</sup> Slightly modified from directions of W. M. Murray and S. E. Q. Ashley, *Ind. Eng. Chem., Anal. Ed.*, **10**, 1 (1938).

## CHAPTER XXXI

### OSMIUM

#### I. Separations

The volatility of osmium tetroxide provides the best method for the separation of osmium from the platinum metals as well as other metals. The procedures that have been described for the distillation of decigram<sup>1</sup> and centigram-milligram<sup>2</sup> quantities of osmium and the recovery of osmium from the distillate do not work well when applied to microgram quantities, and modifications must be introduced. Experiments by the writer have shown that microgram amounts of osmium in the form of the tetroxide or as osmate can be distilled with satisfactory recovery by simply boiling off one-fifth of the original solution (5 *N* in nitric acid). An all-glass distilling apparatus with a water-cooled condenser is used. The distillate is collected in 1:1 hydrochloric acid saturated with sulfur dioxide. Five or ten milliliters of this solution suffice for the collection of the distillate from 50 ml. of the original solution. The evaporation of the hydrochloric acid-sulfur dioxide solution has been found to lead to a loss of osmium, and the element must therefore be determined in this solution without concentration. The presence of sulfur dioxide does not cause interference in the subsequent photometric determination of osmium with thiourea. Although the latter reagent develops a yellow color with sulfurous acid, the transmittancy of the solution is hardly affected if a suitable green filter is used. Reducing substances in the solution from which osmium is to be distilled are destroyed by oxidation in sulfuric acid solution with a slight excess of potassium permanganate. The permanganate remaining and any higher manganese oxides formed are destroyed with a small excess of ferrous ammonium sulfate (about 50 mg. of the hydrated salt). If these are not destroyed, ruthenium will distil with the osmium. By applying the procedure described, quantities of osmium ranging from 7 to 40 $\gamma$  could be recovered to the extent of 90 per cent or better from 50 ml. of solution.

Osmium can be distilled but slowly from solutions in which it is present as chloroosmate, and the presence of chloride should therefore be avoided. If chloroosmate is present, it is preferable to distil from concentrated sul-

<sup>1</sup> R. Gilchrist, *Bur. Standards J. Research*, **6**, 421 (1931); R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

<sup>2</sup> J. J. Russell, F. E. Beamish, and J. Seath, *Ind. Eng. Chem., Anal. Ed.*, **9**, 475 (1937).



furic acid to reduce the time required, or from concentrated sulfuric acid containing a small amount of nitric acid if ruthenium is absent. Osmium is not readily distilled from concentrated sulfuric acid alone if present as bromoosmate. Ruthenium will not distil from a nitric acid solution so long as the nitric acid concentration is less than 40 per cent by volume. The other platinum metals will not pass into the distillate, nor will they interfere with the volatilization of osmium tetroxide.

Osmium (IV) can be isolated by hydrolytic precipitation of the hydrous oxide. A 10 per cent sodium bicarbonate solution is added to the boiling solution until a precipitate appears and suddenly coagulates.<sup>3</sup> A few drops of bromphenol blue indicator solution are added and the addition of bicarbonate continued until the indicator becomes bluish (pH 4).<sup>4</sup> The solution is boiled for 5 minutes, the precipitate filtered off on an inorganic medium and washed with 1 per cent ammonium chloride.

It has been shown that small quantities (a few milligrams) of osmium can be collected in a lead button by fire assay.<sup>5</sup>

## II. Methods of Determination

### A. THE THIOUREA METHOD

Thiourea reacts with osmium as tetroxide or chloroosmate to give a soluble red complex. Chugaev<sup>6</sup> isolated a red compound  $\text{Os}[(\text{NH}_2\text{CSNH}_2)_6]\text{Cl}_3 \cdot \text{OH}$  as one of the reaction products formed when sodium chloroosmate was heated with thiourea in slightly acid solution. This reaction has been used for the detection of osmium;<sup>7</sup> it may also be used for the determination of the element, but hardly any data are available on the quantitative application. The sample solution should be strongly acid and should be free from oxidizing agents. When osmium is present as the tetroxide in 4 N hydrochloric acid solution the color appears very shortly after the addition of thiourea, even at room temperature, and reaches full development in approximately five minutes. On the other hand, when osmium is present as chloroosmate the red color appears only slowly on boiling. The addition of a little stannous chloride produces a rapid development of the color on heating in this case.

Ruthenium gives a blue color with thiourea (p. 388).

<sup>3</sup> Probably a little ferric iron can be added to give ferric hydroxide to gather very small amounts of hydrous osmium dioxide.

<sup>4</sup> The precipitation of osmium is complete in the pH range 1.5-6.3 (Gilchrist).

<sup>5</sup> J. J. Russell, F. E. Beamish, and J. Seath, *Ind. Eng. Chem., Anal. Ed.*, **9**, 475 (1937).

<sup>6</sup> L. Chugaev, *Z. anorg. allgem. Chem.*, **148**, 65 (1925).

<sup>7</sup> L. Chugaev, *Compt. rend.*, **167**, 235 (1918); R. Gilchrist, *Bur. Standards J. Research*, **6**, 421 (1931).

## ¶ Procedure

To 10 ml. of sample solution which is 4 *N* in hydrochloric acid, and which should contain more than 10  $\gamma$  of osmium, add 0.50 ml. of 10 per cent aqueous thiourea solution; if osmium is present as chloro- or bromoosmate also add 0.10 ml. of 10 per cent stannous chloride solution in 1:5 hydrochloric acid. Heat in a tube in a bath of boiling water for 5 minutes if osmium is present as tetroxide and for 10 minutes if it is present in the quadrivalent state. Cool to room temperature and dilute to 25 ml. (or a smaller volume) with water. Determine the transmittancy, using a blue or a green filter.

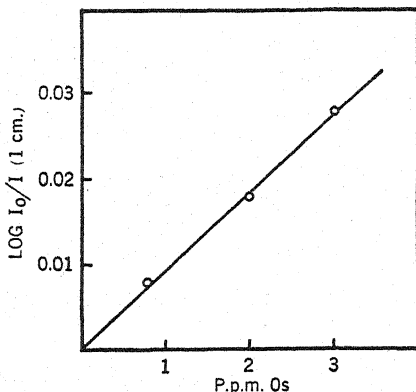


Fig. 48.—Determination of Os (as  $\text{OsCl}_6^-$ ) with thiourea (blue filter, Jena BG-12).

## B. OTHER METHODS

There are various organic compounds that give more or less sensitive color reactions with osmium and may find some quantitative application. Thus the following all react with osmium tetroxide: potassium thiocyanate (blue soluble compound in acid solution, extractable by ether or amyl alcohol),<sup>8</sup> ephedrine hydrochloride (orange color in sodium hydroxide solution, carbon tetrachloride extracts),<sup>9</sup> thiocarbanalide (red color, ether extracts),<sup>10</sup> toluidine, benzidine,<sup>11</sup> and tetramethyl-*p*-phenylenediamine.<sup>12</sup> See also p. 390.

Osmium (and also ruthenium) in the octavalent and quadrivalent states

<sup>8</sup> M. Hirsch, *Chem. Ztg.*, **46**, 390 (1922).

<sup>9</sup> S. O. Thompson, F. E. Beamish, and M. Scott, *Ind. Eng. Chem., Anal. Ed.*, **9**, 421 (1937).

<sup>10</sup> L. Wöhler and L. Metz, *Z. anorg. allgem. Chem.*, **138**, 368 (1924).

<sup>11</sup> N. A. Tananaeff and A. N. Romanjuk, *Z. anal. Chem.*, **108**, 30 (1937). For a color reaction with ferrocyanide see this paper.

<sup>12</sup> L. M. Kul'berg, *J. Gen. Chem. U.S.S.R.*, **8**, 1139 (1938).

strongly catalyzes the reaction between arsenic (III) and cerium (IV) in acid solution, which normally proceeds with extreme slowness.<sup>13</sup> The same reaction is catalyzed by iodine and a photometric method for the determination of iodine based on the rate of reduction of cerium (IV) by excess arsenite has been described.<sup>14</sup> It may be expected that essentially the same method can be applied in the determination of osmium.<sup>15</sup> The catalytic effect of osmium is even stronger than that of iodine, being perceptible with a few thousandths of a microgram of osmium in 5 ml. of solution. Chloride reduces the catalytic power of osmium and its amount in the solution must be controlled.

<sup>13</sup> K. Gleu, *Z. anal. Chem.*, **95**, 385 (1933).

<sup>14</sup> A. L. Chaney, *Ind. Eng. Chem., Anal. Ed.*, **12**, 179 (1940).

<sup>15</sup> J. J. Ivan has shown (unpublished investigation, University of Minnesota, 1940) that traces of osmium can be determined through the agency of its catalytic activity on the reaction mentioned by using the chronometric technique (cf. E. B. Sandell and I. M. Kolthoff, *Mikrochim. Acta*, **1**, 10 (1937)). In this study use was made of the extractability of osmium tetroxide from aqueous solutions by carbon tetrachloride.

## CHAPTER XXXII

### PALLADIUM

#### I. Separations

For the isolation of palladium with the other noble metals by cupellation, reference must be made to the literature.<sup>1</sup> The slight solubility of palladium dimethylglyoxime and other oximes in dilute (0.25 *N*) mineral acid solution enables fairly small amounts of palladium to be separated from most other metals except gold<sup>2</sup> (platinum tends to contaminate palladium dimethylglyoxime). Such precipitation fails at the low palladium concentrations frequently encountered. Possibly the extractability of certain palladium oximes by organic solvents may find application in the separation of traces. Thus, palladium  $\alpha$ -furildioxime can be extracted by chloroform.

Minute amounts of palladium can be coprecipitated with elemental tellurium obtained by reduction of a tellurite with stannous chloride or similar strong reducing agent. Palladium is probably carried down in the precipitate as the telluride. Gold, platinum, and presumably other platinum metals accompany palladium. This method is a very valuable one, because iron, copper, arsenic, etc. do not interfere. Tellurium can be volatilized from the collected precipitate by ignition. The procedure is described in detail on p. 355.

According to Yoe and Overholser,<sup>3</sup> gold can be separated satisfactorily from palladium, preliminary to colorimetric determination of the latter, by extraction of auric chloride from hydrochloric acid solution by ether or ethyl acetate. The latter is said to be the more efficient extractant. The solution to be extracted should have as small a volume as conveniently possible (approximately 10 ml.) and should be about 6 *N* in hydrochloric acid. It is shaken with an equal volume of ether or ethyl acetate, the aqueous layer is drawn off and the organic solvent layer is washed with a few milliliters of 6 *N* hydrochloric acid. The washings are combined with the original solution and the extraction repeated once (for 5–10 mg. gold) or twice (for 20 mg. and more). The concentration of gold should then be reduced to the point where it will not interfere in the colorimetric method

<sup>1</sup> A recent study has been made by J. Seath and F. E. Beamish, *Ind. Eng. Chem., Anal. Ed.*, **12**, 169 (1940).

<sup>2</sup> See, for example, F. E. Beamish and M. Scott, *Ind. Eng. Chem., Anal. Ed.*, **9**, 460 (1937).

<sup>3</sup> J. H. Yoe and L. G. Overholser, *J. Am. Chem. Soc.*, **61**, 2058 (1939).

given on p. 353. The authors mentioned were able to determine 5 or 10  $\gamma$  of palladium in the presence of 10 to 15 mg. of gold with an average error of about 10 per cent.

For the separation of palladium from platinum, the method of Gilchrist and Wichers<sup>4</sup> may be applied, in which palladium is precipitated hydrolytically as the hydrous dioxide. Rhodium and iridium accompany palladium. Yoe and Overholser use ferric hydroxide as a collector for the palladium precipitate. The procedure is as follows. Two or three-tenths of a milligram of ferric iron and 100 mg. of sodium chloride are added to the solution and the latter evaporated to dryness. If the solution contains nitric acid, hydrochloric acid is added and evaporation to dryness carried out several times. The residue is treated with 2-3 drops of hydrochloric acid and dissolved in approximately 25 ml. of water. The solution is heated to boiling and 2 ml. of 10 per cent sodium bromate solution are added, followed by 10 per cent sodium bicarbonate solution until cresol red just turns pink (the indicator is allowed to flow down the stirring rod to mix with adhering drop at the end). Two ml. more of sodium bromate solution are added and the boiling continued for 15 minutes. The precipitate is collected in a porous porcelain or sintered glass filter crucible and washed several times with small portions of hot 1 per cent sodium chloride solution of pH 6-7. The washed precipitate is dissolved in a few milliliters of hydrochloric acid, and if colorimetric determination of palladium according to the method described on p. 353 is to follow, the solution is evaporated to incipient dryness to remove the acid. This procedure permits the quantitative separation of as little as 2  $\gamma$  of palladium from 20 mg. of platinum.

Silver cannot be separated satisfactorily from palladium by precipitation as chloride because of the strong coprecipitation of palladium, unless palladium is first converted into a tetrammine salt. This can be done<sup>5</sup> by treating the hot solution of the nitrates with ammonia until the precipitate first formed redissolves and the solution becomes colorless. The solution is then acidified with acetic acid and treated hot with a slight excess of dilute hydrochloric acid.

## II. Methods of Determination

### A. NITROSOPHENYLAMINO METHOD

Compounds containing the *p*-nitrosophenylamino group, *p*-NOC<sub>6</sub>H<sub>4</sub>N<, form strongly colored complexes with palladous salts.<sup>6</sup> Thus *p*-nitrosodimethylaniline gives the bright red compound Pd[NOC<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub>

<sup>4</sup> R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

<sup>5</sup> W. R. Schoeller and A. R. Powell, *Analysis of Minerals and Ores of the Rarer Elements*. Griffin, London, 1940; p. 261.

<sup>6</sup> L. G. Overholser and J. H. Yoe, *J. Am. Chem. Soc.*, **63**, 3224 (1941).

with palladium chloride in weakly acid solution. Both *p*-nitrosodimethylaniline and *p*-nitrosodiphenylamine may be used for the colorimetric determination of palladium.<sup>6,7</sup> The former reagent is preferable for the determination of palladium in pure solution, since it gives a color that develops more rapidly and is more stable than that given by nitrosodiphenylamine, and moreover it is better suited for a spectrophotometric determination (*cf.* Figs. 49a and 49b). However in practical work the diphenyl compound may be the better reagent because of the higher limiting concentrations of iron, copper, and gold allowed by it. Neither reagent can be used in solutions having high neutral salt concentration (decrease in color intensity), the upper limits being 0.03 and 0.05 *M* in the case of sodium

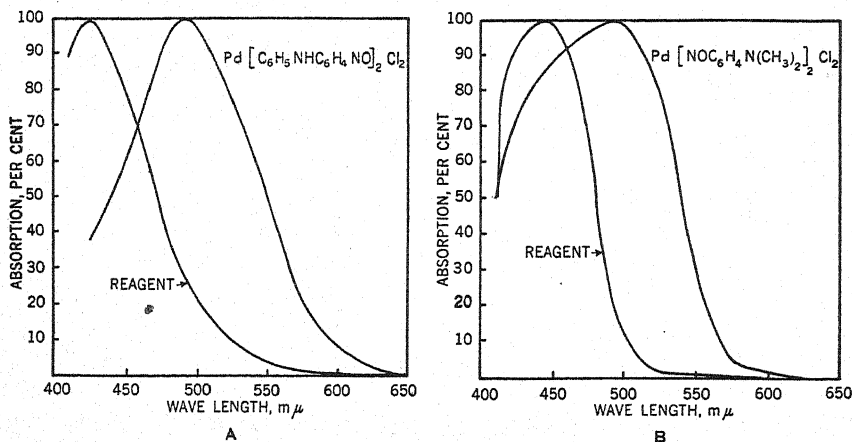


Fig. 49.—Absorption curves of (A) *p*-nitrosodiphenylamine and its complex with  $\text{PdCl}_2$ , and (B) *p*-nitrosodimethylaniline and its complex with  $\text{PdCl}_2$ . (Overholser and Yoe.)

chloride for *p*-nitrosodiphenylamine and *p*-nitrosodimethylaniline respectively. The *pH* of the medium must be regulated fairly closely with both. The palladium complex yielded by nitrosodimethylaniline is more soluble than that given by nitrosodiphenylamine, which explains the longer period of time required for the latter reagent to give the maximum color intensity (formation of a colloidal suspension).

The procedures with the two reagents are similar, the only differences being in the *pH* of the solutions and the time of standing before color comparison. Both procedures are given below. Oxidizing agents, cyanide, and iodide interfere. Quadrivalent platinum does not react with either reagent, but except in small amounts it interferes because of its color, and the same is true for the other platinum metals. Divalent platinum gives a

<sup>7</sup> J. H. Yoe and L. G. Overholser, *J. Am. Chem. Soc.*, **61**, 2058 (1939).

sensitive color reaction with the reagents very similar to that of palladium. Gold reacts in much the same manner as palladium but much less sensitively. Silver naturally interferes except in very low concentrations by giving a turbidity in chloride solutions. Palladium can be determined in the presence of as much as 200 p.p.m. of silver with *p*-nitrosodiphenylamine as reagent by using a mixture of sodium acetate and nitric acid (*pH* 1.2) in place of sodium acetate-hydrochloric acid, and proceeding as described in (2) below.

### 1. General Procedure with *p*-Nitrosodimethylaniline

#### Solutions

*p*-Nitrosodimethylaniline. Dissolve 25 mg. in 50 ml. of 95 per cent ethyl alcohol and dilute to 100 ml. with water.

Sodium acetate—hydrochloric acid mixture. Dilute 80 ml. of 1 *N* hydrochloric acid and 200 ml. of 1 *M* sodium acetate solution to 1 liter with water. The *pH* of the mixture is about 4.8.

Standard palladium solution, 0.001 per cent palladium in ca. 1 *N* hydrochloric acid. The solution may be prepared by dissolving palladium metal in aqua regia and evaporating to dryness several times with hydrochloric acid.

#### ¶ Procedure

The sample solution should be substantially free from neutral salts (p. 352) and should be only slightly acid. Transfer an aliquot containing up to 10  $\gamma$  of palladium to a 50 ml. volumetric flask, add 10 ml. of sodium acetate-hydrochloric acid mixture and 0.5 ml. of *p*-nitrosodimethylaniline solution, dilute to the mark with water, and mix. After 5 minutes determine the extinction of the solution at 525  $m\mu$ . Beer's law is obeyed up to a concentration of 1:5,000,000.

### 2. General Procedure with *p*-Nitrosodiphenylamine

#### Solutions

*p*-Nitrosodiphenylamine. Dissolve 5 mg. in 50 ml. of 95 per cent alcohol and dilute to 100 ml. with water.

Sodium acetate—hydrochloric acid mixture. Dilute 240 ml. of 1 *N* hydrochloric acid and 200 ml. of 1 *M* sodium acetate solution to 1 liter with water.

#### ¶ Procedure

Transfer a suitable amount of sample solution (substantially free from salts (p. 352) and only slightly acid), which may contain up to about 5  $\gamma$  of palladium, to a 50 ml. volumetric flask. Add 10 ml. of sodium acetate-hydrochloric acid mixture and 1 ml. of reagent, and dilute to the mark with water. Mix and allow to stand at room temperature for 30 minutes but not longer than one hour. Obtain the extinction of the solution at 510–525  $m\mu$ .

If the standard series method is used, as little as 1  $\gamma$  of palladium per square centimeter cross-section of solution will produce enough color for maximum accuracy in comparison.

### B. OTHER METHODS

Diethylaminobenzylidenerhodanine reacts with palladium in dilute (*ca.* 0.02 *N*) hydrochloric acid solution to give a slightly soluble red complex which may be made the basis of a colorimetric method. Although very sensitive (in the neighborhood of 0.05  $\gamma$  Pd per square centimeter),

TABLE 49  
DETERMINATION OF PALLADIUM

Addition	Volume ml.	Amount of Te mg.	Pd taken $\gamma$	Pd found $\gamma$
	50	0.5	5.0	4.4
0.5 g. Fe	20	1.0	0.20	0.15
0.5 g. Fe	15	1.0	0.5	0.35
0.5 g. Fe	15	1.0	1.0	0.95
0.5 g. Fe	15	1.0	2.0	1.7
1.0 g. Fe	25	0.5	0.1	0.085
1.0 g. Fe	25	1.0	0.25	0.18
1.0 g. Fe	25	0.5	0.5	0.4
1.0 g. Fe	25	1.0	1.0	0.85
1.0 g. Fe	25	0.5	1.0	1.0
1.0 g. Fe	25	0.5	5.0	4.8
0.5 g. Ni	55	1.0	1.0	0.85
0.5 g. Ni	55	1.0	0.5	0.45
0.5 g. Ni	55	1.0	0.10	0.075
0.5 g. Cu	25	1.0	1.0	0.9
1.0 g. Fe, 0.05 mg. Ag	25	0.5	1.0	0.9
1.0 g. Fe, 0.2 mg. Ag	25	0.5	0.5	0.4
1.0 g. Fe, 2.0 mg. Ag	25	0.5	1.0	0.75
1.0 g. Fe, 1.0 mg. Ag	25	0.5	0.5	0.35

this reaction is not very important from the practical standpoint because gold interferes even in the smallest amounts (p. 252) by giving a very similar color. Silver in small quantities is practically without effect if the reaction is carried out in dilute hydrochloric acid. The acidity has a strong effect and must be carefully regulated.

Iodide develops a brown color with very dilute palladium solutions, but this reaction is of little importance in practical trace analysis.

### III. Applications

Minute quantities of palladium can be determined in sulfide minerals, meteorites, etc. by first isolating the element by coprecipitation with tel-



lurium and then applying the *p*-nitrosodiphenylamine method. Results obtained by the method given below are shown in Table 49. There is a slight loss of palladium in the procedure, but on the whole the results are satisfactory, especially when it is considered that large amounts of iron, copper, nickel, arsenic, etc. may be present. Silver does not interfere to any serious extent if present in amounts of a few tenths of a milligram, but causes low results if present in larger quantities. If the gold content of the sample is less than 50 p.p.m. there is no interference from this element under the conditions of the determination. Small amounts of the other platinum metals are without effect.

### ¶ Procedure

Bring a 0.5 to 1 g. sample (0.1–5 p.p.m. of Pd) into solution by appropriate treatment, as for example with nitric and hydrochloric acids, and remove nitric acid and any other oxidizing agents by repeated evaporation with hydrochloric acid. The final solution may have a volume of 25 to 75 ml. and should be 2 to 3 *N* in hydrochloric acid.

Add sodium tellurite equivalent to 0.5 mg. Te to the solution, and then while stirring or swirling the liquid, add in the cold a 20 per cent solution of stannous chloride dihydrate in 2 *N* hydrochloric acid until a precipitate of tellurium appears, and finally an excess of 3 to 5 ml. for a volume of 50 ml. Heat the solution to boiling, and keep at the boiling point until the precipitate is well coagulated. Filter through a small porous porcelain filter crucible (capacity about 7 ml.), and wash the precipitation vessel and crucible thoroughly with small portions of cold 1 *N* hydrochloric acid. Dissolve the precipitate in approximately 0.5 ml. of warm concentrated nitric acid which has first been poured into the precipitation vessel to dissolve any tellurium in it, followed by 1 ml. of concentrated hydrochloric acid. Allow the mixture to remain in the crucible for a few minutes and then draw it through, collecting the solution directly in a small silica or porcelain crucible. Wash the filter crucible with small portions of hot water.

Add 3 or 4 mg. of potassium sulfate to the combined filtrate and washings and evaporate the solution to dryness. Heat the crucible strongly over a Meker burner for 10 minutes to volatilize all of the tellurium, cool, add a drop of concentrated nitric acid and 2 or 3 drops of concentrated hydrochloric acid, and evaporate to dryness. Add approximately 1.5 ml. of 1:500 hydrochloric acid to the warm crucible, and allow to stand for a few minutes. If the solution is turbid, which is rarely the case, filter it through a small porcelain or sintered glass filter crucible; otherwise transfer it directly to a 20 ml. flat-bottomed tube of about 1.5 cm. internal diameter. Add 50 mg. of potassium pyrosulfate to the crucible, heat at low redness for a few minutes and then strongly for 5 minutes or until practically all

of the pyrosulfate has been decomposed into sulfate. To the cold melt add a drop of nitric acid and two or three drops of hydrochloric acid, evaporate to dryness, and finally heat the residue for about 5 minutes on a low temperature hot plate. Take up the residue in 1 ml. of 1:500 hydrochloric acid, filter through a small porcelain or glass filter crucible, wash with small portions of 1:500 hydrochloric acid, and add the washings to the tube containing the reserved solution. The total volume should be approximately 5 ml. The solution should show no color:

Prepare standards containing suitable amounts of palladium. Each tube should contain the same volume of 1:500 hydrochloric acid as the unknown, and potassium sulfate equivalent to 50 mg. of potassium pyrosulfate. Preferably the added potassium sulfate is obtained by strongly igniting potassium pyrosulfate until practically all of the excess sulfur trioxide has been expelled. To the unknown and standard solutions add 3 ml. of hydrochloric acid-sodium acetate mixture (p. 353) and 0.10 ml. of *p*-nitrosodiphenylamine solution, mix, and compare the colors after one-half to one hour.

## CHAPTER XXXIII

### PLATINUM

#### I. Separations

The metals of the platinum group, together with gold and silver, may be isolated from other elements by the general method of fire assay. This procedure has been used to isolate the most minute amounts of platinum and its congeners not only in sulfide minerals but also in silicates and silicate rocks.<sup>1</sup>

Platinum can be coprecipitated with elemental tellurium obtained by adding a suitable reducing agent to an acid solution containing tellurous acid.<sup>2</sup> The isolation of traces of platinum in this manner has not been studied from the quantitative standpoint, but since it has been shown that minute amounts of palladium (p. 355) and gold (p. 253) can be quantitatively coprecipitated with tellurium thrown down by stannous chloride, it may be expected that platinum will behave in the same manner. The tellurium in the precipitate can be volatilized by strong ignition and the residual platinum brought into solution with aqua regia.

Extraction of chloroplatinous acid with ether or ethyl acetate (p. 359) may be of value at times for separation of platinum from iron, copper, and many other metals.

Little attention has been paid to the separation of small amounts of platinum from large quantities of the other platinum metals. The general procedure for the separation of the platinum metals given by Gilchrist and Wichers<sup>3</sup> should be of service. In this procedure, osmium and ruthenium are first separated by volatilization of the tetroxides, and the residual solution is boiled in the presence of bromate at pH 8 to precipitate the hydrous oxides of palladium, iridium, and rhodium; platinum (IV) is left in solution. The precipitate must be redissolved and the precipitation repeated one or more times.

The separation of gold from platinum can be accomplished by precipitating gold with a reagent such as oxalic acid, sulfur dioxide, nitrous acid, or hydroquinone (p. 247) which does not reduce platinum to the metal (a reprecipitation is required however), or by extracting chlorauric acid with

<sup>1</sup> G. Lunde, *Z. anorg. allgem. Chem.*, **161**, 1 (1927); *Mikrochemie*, **5**, 102 (1927). G. Lunde and M. Johnson, *Z. anorg. allgem. Chem.*, **172**, 167 (1928).

<sup>2</sup> For a study of the detection of platinum based on this separation see S. K. Hagen, *Mikrochemie*, **15**, 180 (1936).

<sup>3</sup> R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

ether or ethyl acetate from a hydrochloric acid solution of Pt (IV) (p. 350). Silver may be separated by precipitation as chloride with a slight excess of hydrochloric acid, if the precipitate is dissolved in ammonia and again thrown down by acidification to release coprecipitated platinum.<sup>4</sup> Platinum will occur in the filtrate from the reprecipitated silver chloride as the ammine compound and in order to convert it into chloroplatinic acid, it is necessary to evaporate the solution, destroy ammonium nitrate with hydrochloric and nitric acids, evaporate to fumes with sulfuric acid and, after elimination of most of the latter, to treat with dilute aqua regia.

For the separation of platinum and the other platinum metals in the silver assay bead, see Beamish and Scott.<sup>5</sup>

Platinum and the other platinum metals except iridium can be adsorbed from very dilute acid solution with activated charcoal. Thus Wölbling,<sup>6</sup> using "carboraffin", was able to reduce the concentration of platinum, palladium, osmium, and ruthenium to  $10^{-8}$  g. per liter of 0.01 *N* hydrochloric acid solution; the concentration of rhodium solution could be reduced to  $10^{-7}$  g. per liter. Unlike the adsorption of gold and silver by charcoal, the adsorption of the platinum metals does not involve reduction to the respective metals, since the platinum metal salts can be washed out of the charcoal with hot concentrated sodium chloride solution or strong hydrochloric acid. The platinum metals are strongly adsorbed by silica gel from ammoniacal solution, but only slightly from acid solution.

According to Wölbling, platinum (and also iridium, rhodium, and ruthenium) can be quantitatively precipitated by ammonium hydroxide if a sufficient amount of ferric iron or aluminum is present.

## II. Methods of Determination

The stannous chloride and the iodide methods for platinum described below have approximately the same sensitivity but the former method has the advantages of being generally freer of interference from other substances and of giving very rapid color development.

### A. THE STANNOUS CHLORIDE METHOD

The yellow color which is obtained when stannous chloride is added to an acid solution of quadrivalent platinum is usually ascribed to chloroplatinous ion. The color intensity depends upon the hydrochloric acid concentration. A suitable final acidity is about 0.25 *N*. For a solution containing 1 p.p.m. of platinum, it was found that the color intensity at a

<sup>4</sup> R. Gilchrist, *J. Research. Natl. Bur. Standards*, **20**, 749 (1938).

<sup>5</sup> F. E. Beamish and M. Scott, *Ind. Eng. Chem., Anal. Ed.*, **9**, 460 (1937).

<sup>6</sup> H. Wölbling, *Ber.*, **67**, 773 (1934); *Angew. Chem.*, **45**, 720 (1932).

hydrochloric acid concentration of 1.25 *N* was three-fourths of that at 0.3 *N*, and at 0.05 *N* the intensity was less than half that at 0.3 *N*. The color development is so rapid at an acidity of 0.3 *N* that constant transmittancy is obtained by the time the solution has been mixed and the first readings can be made. The color is quite stable. Thus a solution containing approximately 1 p.p.m. of platinum gave the following extinctions at various times after the stannous chloride was added (procedure below): 5 minutes, 0.041; 20 minutes, 0.040; 1 hour, 0.040; 2 hours, 0.039; 4½ hours, 0.039; 24 hours, 0.040.

The metal interfering most strongly is palladium, which gives a color nearly as intense as that of platinum.<sup>7</sup> Ruthenium gives a weak color

TABLE 50  
DETERMINATION OF PLATINUM WITH STANNOUS CHLORIDE  
(Final volume 50 ml. Transmittancy determined 5 minutes after mixing.  
Jena filter BG 12)

Pt present γ	Pt found γ
5	6
10	10.5
50	48
50 + 50 γ Pd	83
50 + 50 γ Rh	50
50 + 50 γ Ir	48.5
50 + 50 γ Ru	55.5
50 + 55 γ Au	54
50 + 50 mg. Fe (III) <sup>a</sup>	54
50 + 10 mg. Cu (II)	50

<sup>a</sup> 8 ml. 10% SnCl<sub>2</sub>·2H<sub>2</sub>O solution for reduction.

under the conditions, and produces an error of about +10 per cent if present in an amount equal to platinum. Rhodium and iridium in low concentrations do not interfere seriously. Gold is precipitated as the metal but small amounts can be tolerated as Table 50 shows. Iron and copper in small quantities do no harm. In the presence of copper the platinum solution shows a greenish yellow instead of the normal orange yellow, but if a blue filter is used there is no appreciable error if the copper concentration is less than 200 p.p.m.

Chloroplatinous acid can readily be extracted with ethyl ether and ethyl

<sup>7</sup> H. Wölbling, *Ber.*, **67**, 773, (1934), avoids the interference of palladium by first making the sample solution ammoniacal, adding hydrochloric acid to make the acidity about 1 *N*, and then adding stannous chloride.

acetate<sup>8</sup> if the aqueous solution contains a sufficiently high concentration of hydrochloric acid, namely 1 *N* or greater. If 2 ml. of ethyl acetate are shaken with 10 ml. of a 1:9 hydrochloric acid solution containing 0.5  $\gamma$  of platinum together with stannous chloride in a  $1.8 \times 15$  cm. tube, the organic solvent layer shows a faint but distinct yellow color when examined transversely. Comparison of the color of the ethyl acetate layers of a series of standards with the layer of a sample solution in this manner is a useful method for determining very small quantities of platinum.

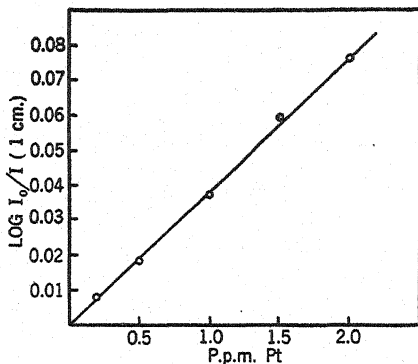


Fig. 50.—Determination of platinum by the stannous chloride method (blue filter, Jena BG-12).

### Special Solutions

*Stannous chloride*, 10 per cent solution of the dihydrate in 2 *N* hydrochloric acid.

*Standard platinum solution*, 0.01 per cent. This is conveniently obtained by dilution of a 0.1 per cent solution prepared as follows. Heat 0.100 g. of pure platinum with few milliliters of aqua regia until all has dissolved and evaporate the solution practically to dryness. Add 5 ml. of concentrated hydrochloric acid and 0.1 g. of sodium chloride and evaporate to dryness. Dissolve the residue in 20 ml. of 1:1 hydrochloric acid and dilute the solution to exactly 100 ml. Dilute this solution with 1:10 hydrochloric acid to give a 0.01 per cent solution.

### Procedure

Transfer the sample solution, containing 25–100  $\gamma$  of platinum, to a 50 ml. volumetric flask, add 10 ml. of 1:10 hydrochloric acid together with enough water to make the volume 30–40 ml. Then add 2.0 ml. of stannous chloride solution, dilute to volume with water, mix, and determine the transmittancy of the solution, using a blue filter. The standards should have the same hydrochloric acid concentration as the sample.

<sup>8</sup> For the use of these extractants in the determination of platinum see N. A. Figurovskii, *Ann. secteur platine, Inst. chim. gén. U.S.S.R.*, No. 15, 129 (1938).

### B. THE IODIDE METHOD

Iodide reacts slowly with chloroplatinate in slightly acid medium to give a rose-colored solution of the iodoplatinate. A high acidity is undesirable because of the increased tendency toward liberation of iodine in such a

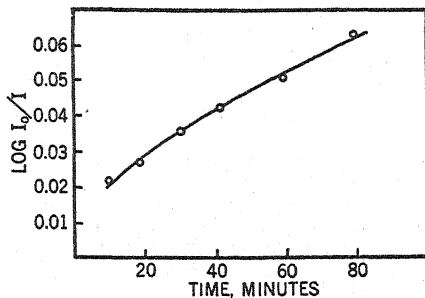


Fig. 51.—Effect of time on color intensity in the iodide method for platinum (ca. 2 p.p.m. of Pt).

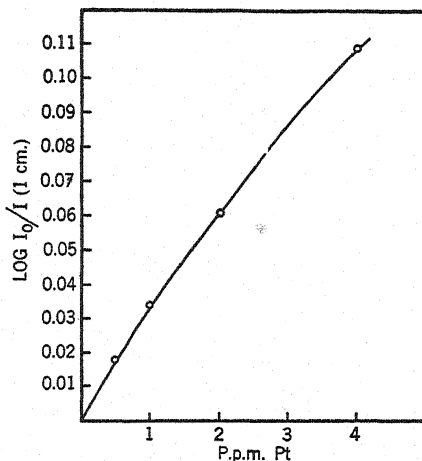


Fig. 52.—Determination of platinum by the iodide method. Transmittancy determined after one hour with a blue-green filter.

medium. The color develops more rapidly if the solution is heated. The following elements, among others, must be absent: palladium, gold, iron, copper, and bismuth. Oxidizing agents liberating iodine as well as reducing agents which reduce quadrivalent platinum must not be present. Rhodium gives a color similar to that given by platinum, but only on long standing (more rapidly on heating).

### ¶ Procedure

Transfer the neutral sample solution containing 25–300  $\gamma$  of platinum (IV) to a 50 ml. volumetric flask and add 1.0 ml. of 1:10 hydrochloric acid and 1.00 ml. of 5 per cent potassium iodide solution. Dilute to volume with water and allow to stand for 1 hour or longer in the dark. Obtain the transmittancy of the solution with a blue-green filter. The standard solutions must be allowed to stand for the same length of time as the sample.



## CHAPTER XXXIV

### POTASSIUM

The methods for the colorimetric determination of potassium are all indirect and require the isolation of the element as some slightly soluble compound containing a constituent capable of giving a strongly colored product with a suitable reagent. Two of these methods in good repute are described below. A third method involving precipitation of potassium as  $\text{K}_2\text{NaCo}(\text{NO}_2)_6$  with sodium cobaltinitrite is usually of inferior accuracy because of the variable potassium/sodium ratio in the precipitate. Depending upon various factors such as the manner of precipitation, the sodium content of the solution, and the composition of the reagent, the ratio K/Na may be greater or less than 2. Under standardized conditions, and with sample solutions not showing too great a variation in sodium and potassium content, useful results can be obtained. Either the nitrite or cobalt content of the precipitate can be determined.<sup>1</sup>

When traces of potassium must be determined in the presence of large amounts of sodium, a preliminary separation from most of the latter will be required and can be obtained by precipitation with sodium cobaltinitrite in cold solution.<sup>2</sup> Separation of potassium as the perchlorate, based on the insolubility of the latter in various organic solvents,<sup>3</sup> should find application in the isolation or concentration of moderately small amounts of potassium in the presence of much sodium as well as of most other metals whose perchlorates are soluble under the conditions. In the determination of traces of potassium in certain heavy metal salts, electrolysis with a mercury cathode is a useful method of removing the heavy metal.

#### Methods of Determination

##### A. DIPICRYLAMINE METHOD<sup>4</sup>

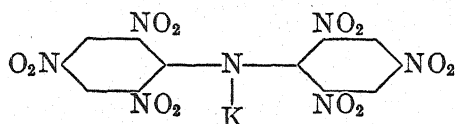
Potassium may be precipitated as the relatively insoluble red dipicrylaminatate (hexanitrodiphenylaminatate) by the addition of lithium, sodium,

<sup>1</sup> For cobaltinitrite procedures see F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*. Van Nostrand, New York, 1936; p. 432. Also W. S. Hoffman, *Photometric Clinical Chemistry*. Morrow, New York, 1941; p. 182.

<sup>2</sup> An even more insoluble precipitate can be obtained by using silver cobaltinitrite as precipitant to give  $\text{K}_2\text{AgCo}(\text{NO}_2)_6$ .

<sup>3</sup> The solubility of potassium perchlorate in ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol, and ethyl acetate is respectively 12, 10, 4.5, and 1.5 mg. per 100 g. of the solvent at 25° according to H. H. Willard and G. F. Smith, *J. Am. Chem. Soc.*, **45**, 286 (1923).

<sup>4</sup> I. M. Kolthoff and G. H. Bendix, *Ind. Eng. Chem., Anal. Ed.*, **11**, 94 (1939); J. Kielland, *Ber.*, **71B**, 220 (1938).



or magnesium dipicrylamine to a neutral or slightly alkaline solution. The precipitate may be washed with ice cold water and a saturated aqueous solution of potassium dipicrylamine, dissolved in acetone, and the solution made up to volume with dilute sodium hydroxide (to repress hydrolysis of the salt). This solution shows maximum absorption below 400 m $\mu$ ; Beer's law is obeyed. The aqueous solution is quite stable, no perceptible change in color intensity occurring in a week.

TABLE 51

TYPICAL RESULTS OBTAINED IN THE COLORIMETRIC DETERMINATION OF POTASSIUM WITH DIPICRYLAMINE<sup>5</sup>

Foreign ion	Potassium taken $\gamma$	Potassium found $\gamma$	Error $\gamma$
	10	9	-1
	30	31	+1
	50	50	0
	100	94	-6
	100	100	0
3 mg. Na	50	48	-2
3 mg. Na	25	36	+11
1 mg. Li	50	50	0
1 mg. Ca	50	54	+4

Rubidium, cesium, and thallium (I), as well as ammonium ion yield slightly soluble dipicrylamines. Certain other metals (lead and mercury) are stated to give crystalline precipitates with sodium dipicrylamine, and many other metals will, of course, be precipitated as hydroxides or basic salts by the alkaline reagent. Small amounts of metals yielding precipitates in basic medium may be removed by boiling the solution with a slight excess of magnesium oxide. Potassium can be determined directly in the presence of moderately large amounts of sodium, lithium, magnesium, and calcium (Table 51). Barium is markedly coprecipitated. The magnesium reagent is not suitable when phosphate is present and sodium dipicrylamine (3 per cent) should then be substituted.

#### Special Solutions

*Magnesium dipicrylamine*, 3 per cent. Add 100 ml. of water to 3 g. of dipicrylamine and 1.3 g. of magnesium oxide, mix well, allow to stand at room temperature for

<sup>5</sup> I. M. Kolthoff and G. H. Bendix, *Ind. Eng. Chem., Anal. Ed.*, **11**, 94 (1939).

15–20 hours and then filter. CAUTION: Dipicrylamine and its salts cause blisters when brought in contact with the skin.

*Wash liquid (1).* Water cooled to 0°C.

*Wash liquid (2).* Add excess potassium dipicrylamine to water at room temperature, immerse the solution in ice water, stir at intervals, and draw off the supernatant liquid by means of a filter stick after a few hours.

## ¶ Procedure

The following directions may be applied in the determination of 0.01 to 0.1 mg. of potassium.

Evaporate the solution to dryness in a suitable vessel, such as a 20 ml. Pyrex beaker. Add 3 drops of magnesium dipicrylamine solution, place the beaker in ice water, and after not less than 15 minutes draw off the supernatant liquid (keep the beaker in the ice bath) with a filter stick, which in this case may advantageously have the form shown in Fig. 53. The filter stick should be cooled to 0° C. before use. Wash the precipitate with 2 drops of wash liquid (1), then with 7–10 drops of wash liquid (2) (cooled to 0°), and finally with one drop of wash liquid (1).

Dissolve the precipitate in the filter stick by filling the portion above the asbestos with acetone (use a medicine dropper) and forcing the latter into the beaker in which the precipitation was made; repeat until the acetone runs through colorless. Dilute the acetone to 50–100 ml. (or any other convenient volume) with approximately 0.001 *N* sodium hydroxide solution in water. Compare or determine the color intensity in any convenient way. In transmission measurements use light of wave length 400  $m\mu$  or a suitable filter transmitting a narrow band in the blue or violet.<sup>6</sup> The standard solutions for comparison or the construction of the standard curve are prepared in the same manner as the sample solution.

**Notes.**—1. According to Amdur (loc. cit.) it is not necessary to carry out the precipitation at 0°. One can work at room temperature if the reagent and wash solution have been saturated with potassium dipicrylamine at the temperature at which the precipitation is made. By precipitating at room temperature, and omitting the washing with water, Amdur determined 100  $\gamma$  of potassium with the respective errors 0, 0, and + 1 per cent, and 50  $\gamma$  with errors of + 1 and + 2 per cent.

2. If the amount of potassium is not too small, it may be determined indirectly by finding the amount of dipicrylamine remaining in solution after precipitation. A procedure has been given by Amdur.<sup>6</sup>

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<sup>6</sup> E. Amdur, *Ind. Eng. Chem., Anal. Ed.*, **12**, 721 (1940), recommends a filter composed of 5.5 mm. of Corning glass No. 556 and 3.8 mm. of Corning No. 429. This filter gives practically a linear relation between extinction and concentration over a wide range of dipicrylamine concentration.

B. CHLOROPLATINATE METHOD<sup>7</sup>

The gravimetric determination of potassium as chloroplatinate, based on the very slight solubility of the salt in alcoholic solution, has long been regarded as the standard method for macro and micro quantities of the element. Instead of weighing the precipitate one can readily determine its amount by dissolving it in water, adding stannous chloride, and measuring the intensity of the yellow color due to  $\text{PtCl}_4^-$ . Potassium iodide may be used in place of stannous chloride to give a wine-red solution ( $\text{PtI}_6^-$ ), but then the solution must be allowed to stand for some time, since the color with iodide develops slowly.

The solubility of potassium chloroplatinate in alcohol-water solutions at 20° is as follows:<sup>8</sup>

Weight Per cent $\text{C}_2\text{H}_5\text{OH}$	Gram $\text{K}_2\text{PtCl}_6$ in 100 g. solution
100	0.0009
90	0.0025
80	0.0085
70	0.0128

The precipitate of potassium chloroplatinate may be washed with 95 per cent alcohol saturated with the salt, after freeing the precipitate as much as possible from chloroplatinic acid. The temperature coefficient of solubility of potassium chloroplatinate in alcohol is small.

## Apparatus

The precipitation and filtration of less than 1 mg. of potassium chloroplatinate is best made by micro-technique. The precipitate can be collected by centrifugation or by filtration with the use of a filter-stick. A Pyrex filter stick with an asbestos plug, such as illustrated in Fig. 53, will be found very suitable. As precipitation vessel, a 5 or 10 ml. Pyrex beaker of ordinary form will serve.

The apparatus illustrated in Fig. 54 is recommended for filtration. It consists of a wide-mouth belljar (which may be obtained by cutting an ordinary 250 ml. wide-mouth bottle about 9 cm. from the top and grinding the cut edge smooth) resting on a plate

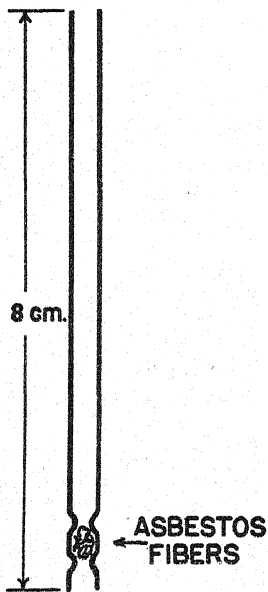


Fig. 53.—Filter stick for use in the determination of potassium as dipicrylamine.

<sup>7</sup> For the application of the chloroplatinate method to the determination of potassium in biological samples see R. M. Tenery and C. E. Anderson, *J. Biol. Chem.*, **135**, 659 (1940); P. W. Salit, *ibid.*, **136**, 191 (1940).

<sup>8</sup> E. H. Archibald, W. G. Wilcox, and B. G. Buckley, *J. Am. Chem. Soc.*, **30**, 747 (1908).

of ground glass. If the surfaces are well ground it will not be necessary to use a lubricant on the plate to render the jar sensibly air-tight. The left-hand tube is connected to a suction line. The other tube should have a narrow bore and its ends should be drawn down as shown. The filter stick is connected by means of a short section of narrow rubber tubing.

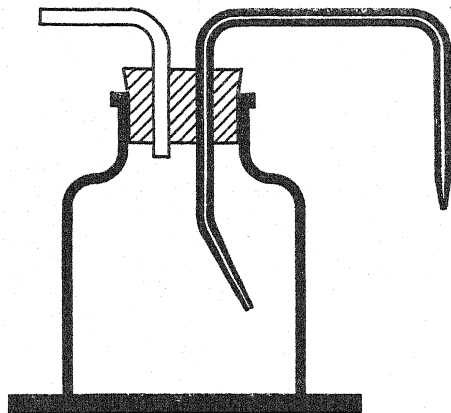


Fig. 54.—Apparatus for filtration with a filter stick.

#### Reagents

*Chloroplatinic acid*, 5 per cent platinum.

*Ethyl alcohol*, saturated with potassium chloroplatinate. Shake 95 per cent alcohol with a small amount of pure potassium chloroplatinate at room temperature (preferably at the same temperature that the precipitation is made). Prepare only enough solution for daily use.

*Stannous chloride*, 10 per cent solution of the dihydrate in 2 *N* hydrochloric acid.

*Standard potassium solution*, 0.100 mg. K (0.191 mg. KCl) per ml.

#### Procedure

The solution may conveniently contain from 0.02 to 0.3 mg. of potassium. Evaporate to a volume of a few drops, add 0.2 ml. of chloroplatinic acid, and evaporate to the point where a moist residue remains. Cool to room temperature and add 2 or 3 ml. of 95 per cent alcohol. Allow to stand covered at room temperature for 30 minutes, stirring at intervals. Draw off the liquid as completely as possible with a filter stick, and add *ca.* 0.5 ml. of alcohol saturated with potassium chloroplatinate in such a manner as to rinse the walls of the precipitation vessel. Draw off the alcohol and repeat the washing 2 or 3 times more. Allow the alcohol to evaporate completely, hastening the process if desired by warming at about 50°.

Add 5 ml. of hot water to the precipitation vessel to dissolve the precipitate and draw the solution through the filter stick over into a small beaker.

Wash with hot water until it is certain that all of the salt has been removed. Cool the solution to room temperature and transfer to a 25 ml. volumetric flask. Add 5 ml. of 1:10 hydrochloric acid, dilute to about 20 ml. if necessary, and add 1.0 ml. of stannous chloride. Dilute to volume and obtain the extinction of the solution, using a blue filter. Obtain the standard curve by carrying known amounts of potassium through the procedure.

The above procedure can be used to determine potassium in the presence of comparable amounts of sodium. The upper limit of the quantity of sodium that may be present has not been ascertained.

**Note.**—If it is desired to use iodide instead of stannous chloride to develop a color with platinum, acidify the aqueous solution of potassium chloroplatinate with 1 ml. of 1:10 hydrochloric acid, dilute to about 20 ml., add 1.0 ml. of 5 per cent potassium iodide solution, make up to 25 ml. and allow to stand for 1 hour in the dark before determining the transmittancy with a blue-green filter.

## CHAPTER XXXV

### THE RARE EARTH ELEMENTS

#### I. Separations

The isolation of the rare earth elements has been investigated by Noddack<sup>1</sup> in connection with their determination in meteorites by X-ray spectrography. Since the procedure is of more or less general application and since it is stated that amounts of the rare earth elements in the range 1-10 p.p.m. can be quantitatively isolated in this way, an outline of the Noddack procedure will be given. The silicate sample (100 g.) is treated with hydrofluoric acid and evaporated to dryness to eliminate silica. The residue is evaporated to fumes several times with sulfuric acid to remove fluorine, and water is added to extract all soluble matter. The mixture is filtered and the filtrate (solution 1) reserved. The residue (1) consists chiefly of calcium sulfate containing a sizeable fraction of the total amount of the rare earths present. The calcium sulfate residue is boiled with sodium carbonate to transform it into calcium carbonate which is filtered off and dissolved in hydrochloric acid. To this solution is added the hydrochloric acid solution of the ammonia precipitate which has obtained from the filtrate from the calcium carbonate precipitation by acidifying and adding an excess of ammonia. The combined solutions are precipitated with ammonia to throw down iron, chromium, etc. together with the rare earths. The precipitate is dissolved in acid and the ammonia precipitation repeated to eliminate calcium. The precipitate is dissolved in acid and the solution (2) reserved.

The main solution (1), containing magnesium, most of the iron, aluminum, nickel, chromium, the rare earths, etc. is treated with ammonia to separate iron and the other precipitable elements from calcium, magnesium and nickel. The precipitate is dissolved and again thrown down. The hydroxides of iron, the rare earths, etc. are dissolved in hydrochloric acid and iron is removed by extraction of ferric chloride with ether from the acid solution. The metals remaining in solution are precipitated with ammonia, and aluminum is dissolved out of the precipitate with dilute sodium hydroxide. The residue is dissolved in acid, chromium is oxidized to the sexivalent state, and an ammonia precipitation made to separate the rare earths and other precipitable elements from chromium. The slightly acid solution of the precipitate is treated with hydrogen sulfide to precipitate lead and other sulfide-forming elements. Then another ammonia precip-

<sup>1</sup> Ida Noddack, *Z. anorg. allgem. Chem.*, **225**, 337 (1935).

itation is made to separate any manganese that may still be present. The solution of the precipitate of the hydrous oxides is combined with solution (2) above.

This solution contains all of the rare earth elements together with more or less iron and manganese, and most of the titanium originally present. Titanium is volatilized by repeated evaporation with hydrofluoric acid, and most of the residual iron is removed by ether extraction of ferric chloride. The rare earths are thus left with a few milligrams of the major constituents of the sample. By repetition of the precipitations in a very small volume, practically all of the remaining amounts of most of the foreign elements can be eliminated; or, the rare earths can be precipitated as the fluorides or oxalates (see below).

The method of concentration described above depends upon the precipitation of the rare earth hydroxides by ammonia, with a slightly soluble hydrous oxide such as that of iron.<sup>2</sup> Other important separation reactions are those with oxalic and hydrofluoric acids. The oxalates and fluorides of the rare earth elements and thorium are but slightly soluble in dilute solutions of the respective acids. Fluoride precipitation gives more complete separation than oxalate precipitation. Ferric iron, titanium, zirconium, aluminum, uranium (VI), columbium, and tantalum remain in solution when an excess of hydrofluoric acid is used. When it is a matter of precipitating the rare earth elements as fluorides or oxalates from very dilute solutions, a collector must obviously be used. The corresponding slightly soluble calcium or strontium salts should be suitable collectors. The trivalent ionic radii (Goldschmidt) in the series La—Eu range from 1.22 to 1.13 Å., and in the series Gd—Lu from 1.11 to 0.99 Å. (the radius of yttrium ion is 1.06 Å). The ionic radii of calcium and strontium are respectively 1.06 and 1.27 Å. It is known that calcium and yttrium fluorides form mixed crystals. Strontium fluoride may be expected to be better than calcium fluoride for gathering lanthanum fluoride. These fluoride precipitates are not very easy to filter and wash. The oxalate precipitates are easier to handle, and should also be useful for collecting the rare earth metals, but few data on this point are available.<sup>3</sup>

<sup>2</sup> The rare earth hydroxides (especially of the more basic earths) require an excess of ammonia for complete precipitation, and much ammonium salt is harmful (R. C. Wells, quoted in W. R. Schoeller, *Analytical Chemistry of Tantalum and Niobium*. Nordeman, New York, 1937; p. 166). Low concentrations of the elements cannot be precipitated unless a collector is used. Solutions should be cooled before filtration. Tannin facilitates the hydroxide precipitation (Schoeller). In sodium hydroxide solution some of the rare earth hydroxides (lutecium, also scandium) are appreciably soluble.

<sup>3</sup> I. D. Borneman-Starynkevich, S. A. Borovik, and I. B. Borovskii, *Doklady Akad. Nauk, S.S.S.R.*, **30**, 227 (1941), have isolated the rare earths as a group by coprecipita-



Among other separation methods possibly useful for isolating small amounts of the rare earth elements, there may be mentioned the extraction of the thiocyanates from aqueous solution with butyl alcohol.<sup>4</sup>

## II. Methods of Determination

For the determination of cerium (IV) see p. 185.

### A. BY THE COLORS OF THE RARE EARTH IONS IN AQUEOUS SOLUTION

Solutions of lanthanum, cerium (III), gadolinium, terbium, and yttrium salts are colorless, showing no appreciable absorption in the range 350–1000 m $\mu$ . The other elements show more or less strong absorption bands in this range (*cf.* Fig. 5, p. 34) and can thus be determined spectrophotometrically. A very narrow band of wave lengths must be used, because the absorption maxima of the solutions of the rare earth salts are very sharp. Unfortunately the sensitivity is not great, so that the method is of limited value in trace analysis. The original sample must be large if this method is to be applied to material low in the rare earths. The spectrophotometric method has been carefully studied by Rodden,<sup>5</sup> who used solutions of the rare earth nitrates. See the summary in Table 52. Beer's law is generally followed. Deviations that are observed with praseodymium and samarium may be due to insufficiently monochromatic light. Slight absorption by another rare earth at the wave length at which the element being determined absorbs strongly may be corrected for by finding the amount of the interfering element from its absorption at the wave length of minimum transmittancy.<sup>6</sup>

### B. BY FLUORESCENCE

Various members of the rare earth group can be detected and determined by the fluorescence exhibited in liquid and solid solution. Both trivalent and divalent rare earth ions fluoresce under suitable conditions of excitation. The fluorescence of the trivalent ions will be considered first. Hait-

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tion with calcium oxalate preparatory to determination spectrographically (in soils and plant ash). H. Lux, *Z. anorg. allgem. Chem.*, **240**, 21 (1938), also made use of calcium oxalate as a collector for the rare earth elements in determining them in bones. A lengthy procedure was then followed in removing phosphate, calcium, iron, etc. Only about one-third of the original quantity of the earths was recovered. W. O. Robinson, *Soil Sci.*, **56**, 1 (1943), applied oxalate precipitation of the rare earths in isolating them from plant ash and soil.

<sup>4</sup> D. B. Appleton and P. W. Selwood, *J. Am. Chem. Soc.*, **63**, 2029 (1941).

<sup>5</sup> C. J. Rodden, *J. Research Natl. Bur. Standards*, **26**, 557; **28**, 265 (1942).

<sup>6</sup> See the transmission curves given by Rodden.

inger<sup>7</sup> made use of the fluorescence of certain of the rare earths in borax or phosphate beads for their detection. An iron arc was used for excita-

TABLE 52  
SPECTROPHOTOMETRIC DETERMINATION OF THE RARE EARTH METALS AS NITRATES

Element	Suitable wave lengths $m\mu$	Sensitivity $\gamma/cm^2 = 0.001E$	Remarks
Pr	446	23	Sm absorbs at this wavelength, but Nd only slightly.
Nd	521		Less sensitive than 798 $m\mu$ .
	798	9	Pr and Sm do not interfere.
Sm	402	45	Nd and Pr interfere slightly.
Eu	396	150	Sm must be absent.
Dy	910	50	Ho, Yb and Er (slightly) absorb at this wave length.
Ho	643	50-60	Tm and especially Er absorb.
Er	521	90	Ho and Tm (slightly) absorb.
	653	90	Tm and especially Ho absorb.
Tm	684	40-50	Ho and Er absorb slightly.
Yb	950	—	Dy and Er (slightly) absorb; less sensitive than 973 $m\mu$ .
	973	50	Dy absorbs (less than at 950 $m\mu$ ).

TABLE 53  
FLUORESCENCE OF THE RARE EARTH ELEMENTS IN BORAX BEADS EXCITED WITH AN IRON ARC

Element	Character of spectrum	Limiting concentration in bead
Ce	Continuous, maximum intensity at 450 $m\mu$	1:10,000
Eu	Three bands in red, orange and yellow	1:500
Sm	Bands in red (2), orange, yellow, green and blue-green	1:1000
Tb	Bands in red, orange, green, and blue-green	1:5000
Dy	Narrow band in orange, broad band close by in yellow	1:1000
Tm	Broad band in the blue	
Ho	As for Dy, but weaker	

tion. Cerium is the only element of the cerium earths that fluoresces; it gives a blue color in a borax bead. Europium, samarium, and gadolinium

<sup>7</sup> M. Hätinger, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. IIA*, **142**, 339 (1933).

give strong red, reddish yellow, and orange-yellow colors respectively. Dysprosium fluoresces an intensive yellow, thulium a violet-blue, and holmium a weak yellow. Cf. also Table 53. No fluorescence was noted with lanthanum, praseodymium, erbium, ytterbium, and lutecium. Metals other than the rare earths show a fluorescence in the borax bead according to Haitinger—copper and gold yellow, manganese rose and tin light yellow; the fluorescence spectra of these are continuous. In addition, a yellowish green fluorescence is shown by uranium under the same conditions (cf. p. 433).

For the detection of the rare earths by fluorescence after incorporation in calcium tungstate see the work of Servigne.<sup>8</sup>

Terbium, cerium, and europium may be determined in *aqueous solution* by their fluorescence spectra; the respective limits are  $10^{-6}$ ,  $10^{-5}$ , and  $10^{-2}$  per cent.<sup>9</sup> Gadolinium gives only a weak fluorescence.

Przibram and others<sup>10</sup> have studied the fluorescence of divalent rare earth ions in the lattice of calcium fluoride and other substances. Europium (II) in calcium fluoride shows a blue fluorescence (center of band at  $429\text{ m}\mu$ ), and ytterbium (II) in the same host gives a yellow-green fluorescence ( $570\text{ m}\mu$ ) at liquid-air temperature. The divalent ions may be obtained by exposing the preparation to radium radiation and also to X-rays and short-wave ultraviolet. Divalent europium in sodium chloride also gives a blue fluorescence. In this case it suffices to heat the sodium chloride crystals (obtained by evaporation from a solution containing trivalent europium) to  $300^\circ$  to reduce the europium and produce fluorescence on exposure to ultra violet radiation from a quartz lamp. The limit of detection of europium by this procedure is of the order  $10^{-6}$ . Since the fluorescence can readily be observed with 1 mg. of sodium chloride, as little as  $0.001\text{ }\gamma$  of europium is detectable. Samarium (II) in anhydrous calcium sulfate, exposed to radium radiation, shows a red fluorescence band ( $619\text{ m}\mu$ ). The limit of detectability is  $5 \times 10^{-8}$ . The limit is even lower with calcium fluoride, for it was found that calcium fluoride prepared from the purest calcium salt still gave a red fluorescence. Thulium in calcium sulfate gives a red fluorescence (same band position as for samarium) at liquid-air temperature. One part of thulium in  $10^8$  parts of calcium sulfate gives a distinct fluorescence. It remains to be seen what practical analytical use can be made of these interesting phenomena.

<sup>8</sup> M. Servigne, *Ann. chim. anal. chim. appl.*, **22**, 273 (1940).

<sup>9</sup> A. Zaidel, Y. Larionov, and A. N. Filipov, *J. Gen. Chem. U.S.S.R.*, **8**, 943 (1938).

<sup>10</sup> K. Przibram, *Mikrochim. Acta*, **3**, 69 (1938); further references will be found in this paper.

## C. OTHER METHODS

Various lake-forming reagents may be used for the detection, and presumably for the determination, of the rare earth elements. For example, addition of quinalizarin, followed by sodium hydroxide, to a rare earth solution produces a blue color, or blue precipitate. The following approximate limiting concentrations have been found:<sup>11</sup> Ce, 1:1,000,000; La, 1:500,000; Nd, 1:2,000,000; Pr, 1:1,000,000; Th, 1:150,000; Zr, 1:150,000 (all on the test tube scale).

Cochineal has been recommended as a color reagent for the rare earths.<sup>12</sup> When cochineal tincture is added to a neutral earth solution, a red-violet color is obtained. Thorium gives a blue color, and various other metals also react with the production of different colors or colored precipitates. The limiting concentration for the rare earth metals is stated to be 10  $\gamma$  per ml. On addition of dilute acetic acid, the violet color becomes reddish orange with the cerite earths (lanthanum-samarium). Terbium and the erbium earths require stronger acetic acid to change the violet color to red, and a change to the original reddish orange of the cochineal takes place only when quite concentrated acetic acid is used.

<sup>11</sup> A. S. Komarovskiy and I. M. Korenman, *Z. anal. Chem.*, **94**, 247 (1933).

<sup>12</sup> G. Becke, *Mikrochemie ver. Mikrochim. Acta*, **27**, 49 (1939).

## CHAPTER XXXVI

### RHENIUM

Considerable work has been done on the colorimetric determination of rhenium, and satisfactory methods now exist for its determination, particularly in the presence of molybdenum.

#### I. Separations

The outstanding method for the separation and isolation of small amounts of rhenium is based on volatilization of the element as the heptoxide from a hot acid solution of high boiling point. The volatilization or distillation can be carried out in a number of ways. In one procedure (described on p. 381) a sulfuric acid solution is steam distilled at 270° C.,<sup>1</sup> and in another, a sulfuric acid or perchloric acid solution containing hydrochloric acid is distilled.<sup>2</sup>

Small amounts of molybdenum may accompany the rhenium into the distillate, apparently mainly as a result of mechanical carrying over. The colorimetric method used in the subsequent determination must therefore be one in which small amounts of molybdenum may be tolerated.

The only extraction method that has been found useful in effecting a fairly sharp separation of much molybdenum from minute quantities of rhenium makes use of the reduction of molybdenum to the quinquevalent condition by mercury in a solution of regulated acidity and the extraction of molybdenum (V) thiocyanate by ether. Rhenium is not reduced and remains in the aqueous phase. This procedure is the basis of the colorimetric determination given below (p. 378) and details will be found there. Joint isolation of small quantities of molybdenum and rhenium can be carried out by ether extraction after addition of thiocyanate and stannous chloride (see p. 383).

For the isolation of small amounts of rhenium in the distillate obtained by the procedure mentioned above, hydrogen sulfide precipitation with arsenic sulfide as collector may be used. Hoffman and Lundell<sup>2</sup> give the following directions. Neutralize the distillate (100 ml.) with ammonia, add 3 ml. of concentrated sulfuric acid and 5 mg. of trivalent arsenic, and

<sup>1</sup> C. F. Hiskey and V. W. Meloche, *Ind. Eng. Chem., Anal. Ed.*, **12**, 503 (1940); L. C. Hurd and C. F. Hiskey, *ibid.*, **10**, 623 (1938). The distillation method of Geilmann and Weibke, *Z. anorg. allgem. Chem.*, **199**, 120 (1931), involves passage of a mixture of hydrogen chloride and carbon dioxide through a strong sulfuric acid solution.

<sup>2</sup> J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **23**, 497 (1939).

saturate with hydrogen sulfide. Allow the solution to stand overnight, then filter, and without washing, dissolve the precipitate in ammonium hydroxide containing hydrogen peroxide. Evaporate to dryness and determine rhenium according to IIA.<sup>3</sup>

In preparing samples for analysis the possibility of loss of rhenium by volatilization of the heptoxide must be borne in mind. Such loss may occur from hot sulfuric and perchloric acid solutions above *ca.* 200°, and from acid melts. It appears that there is no loss from boiling hydrochloric or nitric acid solutions.

## II. Methods of Determination

### A. THIOCYANATE METHOD

When an acid solution of perrhenate is treated with thiocyanate and stannous chloride a yellowish color appears,<sup>4</sup> which has been ascribed to the formation of  $\text{ReO}(\text{CNS})_4$ . This reaction is very similar to the one given by molybdenum under the same conditions, and there is no satisfactory procedure available for the direct determination of minute amounts of rhenium in the presence of much molybdenum by this reaction.<sup>5</sup> A neat method for separating molybdenum and rhenium and determining the latter has been described by Hoffman and Lundell.<sup>6</sup> In this method, which has already been referred to above, an approximately 2 *N* hydrochloric acid solution of molybdenum (VI) and rhenium (VII) is treated with thiocyanate and shaken with mercury and ether. The molybdenum is reduced and forms molybdenum (V) thiocyanate which is extracted by the ether (the presence of a little iron aids in the extraction of the molyb-

<sup>3</sup> The reliability of this procedure is attested by the following results obtained by Hoffman and Lundell. In one analysis, 10  $\gamma$  of rhenium were added to the distillation flask and 20  $\gamma$  molybdenum to the resulting distillate; 9  $\gamma$  of rhenium were found. In another trial, 5  $\gamma$  of rhenium (with 200  $\gamma$  added molybdenum) were taken and 4.5  $\gamma$  found.

<sup>4</sup> W. Geilmann, F. W. Wrigge, and F. Weibke, *Z. anorg. allgem. Chem.*, **208**, 217 (1932).

<sup>5</sup> If the ratio of molybdenum to rhenium is not too unfavorable, the effect of the molybdenum can to a large extent be eliminated by making use of the greater stability of the rhenium complex in strongly acid solution. In a solution having an optimum concentration of 5 *N* in hydrochloric acid and approximately 9 *N* in sulfuric acid, the color of the molybdenum complex fades fairly rapidly whereas that of the rhenium complex remains relatively unchanged (see L. C. Hurd and C. F. Hiskey, *Ind. Eng. Chem., Anal. Ed.*, **10**, 623 (1938)). C. F. Hiskey and V. W. Meloche, *ibid.*, **12**, 503 (1940), were able to determine 100  $\gamma$  Re in the presence of 5 to 10 mg. Mo by this method with an error of *ca.* +10 per cent by comparing after 60–75 minutes, and with an error of *ca.* + 5 per cent after 90 minutes.

<sup>6</sup> J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **23**, 497 (1939).

denum). Rhenium remains largely unchanged<sup>7</sup> in the aqueous layer, and can be determined by the addition of stannous chloride and extraction of the Re (VI) thiocyanate complex with ether. The color of the rhenium complex is fairly stable; a solution in ether having a concentration of 1 mg. Re per liter faded 2.5 per cent in 2 days, and another containing 5 mg. per liter increased in color intensity by 0.5 per cent. Slight deviation from Beer's law is shown by rhenium thiocyanate solutions in ether, but this may be due to the slight instability of the solutions rather than to true deviations. Butyl acetate may be used instead of ethyl ether in the extraction but has no particular advantages.

Among the non-interfering elements in the procedure the following are included: cerium, cobalt, chromium, gallium, germanium, indium, iridium,

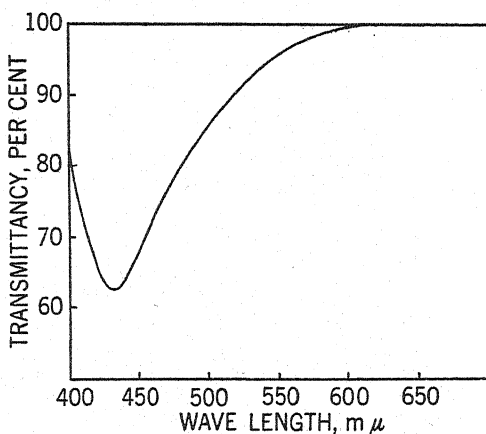


Fig. 55.—Transmission curve of rhenium thiocyanate in ether (1.07 p.p.m. Re, 1 cm. cell, 2 day-old solution). (Hoffman and Lundell.)

lead, nickel, osmium, ruthenium, thallium, uranium, and vanadium (all in 2 mg. quantities). Chromium in large amounts (40 mg.) imparts a slight green tint to the ether. Platinum, rhodium and tungsten interfere by coloring the ether layer. Copper, gold, palladium, selenium, and tellurium do not color the ether, but they separate and contaminate the mercury.

The determination of rhenium in pure solution has been studied by Hurd and Babler,<sup>8</sup> who recommend that the concentration of hydrochloric acid be 2 per cent, of potassium thiocyanate 0.4 per cent, and of stannous chlo-

<sup>7</sup> Under the conditions prescribed in the procedure following, a small proportion of the rhenium, varying from 1 to 5 per cent passes into the ether with the molybdenum.

<sup>8</sup> L. C. Hurd and B. J. Babler, *Ind. Eng. Chem., Anal. Ed.*, **8**, 112 (1936).

ride 0.2 per cent, that the mixture be allowed to stand 7 minutes before extraction with ether, and that shaking not be unnecessarily prolonged.

The procedure of Hoffman and Lundell follows.

### Special Solutions

*Potassium thiocyanate*, 20 per cent.

*Stannous chloride*. Dissolve 35 g. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 20 ml. of 1:1 hydrochloric acid and dilute to 100 ml. with water.

*Ether for dilution*. To 100 or 200 ml. of ethyl ether in a separatory funnel add 25 ml. of 1:4 hydrochloric acid, 2 ml. 20 per cent potassium thiocyanate solution, and about 10 g. of mercury. Shake vigorously for one minute. Draw off the mercury and acid and reserve the ether.

*Standard rhenium solution, 0.01 or 0.001 per cent Re*. Dissolve 0.0155 g. of pure potassium perrhenate in water, add 5 ml. of 6 *N* sulfuric acid and dilute to 100 ml. with water (1 ml. = 100  $\gamma$  Re). From this solution prepare one containing 10.0  $\gamma$  Re per ml. by dilution with ca. 0.3 *N* sulfuric acid.

TABLE 54  
DETERMINATION OF RHENIUM IN THE PRESENCE OF MOLYBDENUM BY THE  
THIOCYANATE METHOD OF HOFFMAN AND LUNDELL<sup>9</sup>

Molybdenum present mg.	Rhenium present $\gamma$	Rhenium found $\gamma$
10	1.0	0.9
10	5.0	4.8
10	10.0	10.9
5	80	78
10	100	97

### Procedure

The sample may contain as much as 10 mg. of molybdenum and as little as 1  $\gamma$  of rhenium.

**Separation of Molybdenum and Rhenium.**—Evaporate the sample solution to practical dryness and add about 10 mg. of iron as ferric chloride (if iron is not already present) and 1–2 drops of saturated potassium permanganate solution. Add a slight excess of ammonia and heat on the steam bath for a few minutes to make certain that molybdenum and rhenium are present in their highest valences (VI and VII respectively). Dissolve the residue in 25 ml. of cool 1:4 hydrochloric acid and 2 ml. of potassium thiocyanate solution. Transfer the solution to a separatory funnel containing 25 g. of mercury. At once add 20 ml. of analytical grade ethyl ether and shake until the aqueous solution becomes colorless (or until the color of ferric thiocyanate has disappeared if chromium, nickel, etc. are

<sup>9</sup> Results obtained by J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **23**, 497 (1939).



present); usually 1 minute of shaking suffices. Allow the phases to separate, and draw off the mercury and aqueous layer into another separatory funnel. Add to the latter 1 ml. of potassium thiocyanate and 15 ml. of ether, shake vigorously for a minute, and draw off the mercury and acid solution as before. Again add 1 ml. of potassium thiocyanate and 15 ml. of ether to the funnel containing the mercury and the aqueous solution, and shake vigorously. Deliver the mercury and aqueous layer into a separatory funnel. If the ether layer is colorless or very nearly so, the extraction of molybdenum is complete; if the ether shows an appreciable color, the aqueous solution must be extracted once more. When all the molybdenum has been removed, separate the mercury from the aqueous solution containing the rhenium.

**Determination of Rhenium.**—To the acid solution from which the mercury has been withdrawn, add 1 ml. of potassium thiocyanate solution and 1 ml. of stannous chloride solution, mix, and allow to stand for 5 minutes. Add 20 ml. of ether, shake vigorously, allow the phases to separate, and run the aqueous layer into another separatory funnel. Repeat the extraction with ether twice, using 15 ml. portions. Discard the acid solution. Combine the ether extracts, shake well with 10 ml. of 1:4 hydrochloric acid (to remove iron which might otherwise oxidize and give a pink color) and run the ether into a 50 ml. volumetric flask. Dilute to the mark with the specially prepared ether.

Prepare the standards for comparison or for the construction of the standard curve as follows. Transfer the standard rhenium solution to a separatory funnel containing 10 mg. of iron as ferric chloride and 25 ml. of 1:4 hydrochloric acid. Add 2 ml. of potassium thiocyanate and 1 ml. of stannous chloride solution. Mix, allow to stand for 5 minutes, and then proceed with the extraction of the rhenium thiocyanate complex as described in the preceding paragraph.

Determine the extinction of the ether solutions at  $432\text{ m}\mu$  (an extinction of 0.001 corresponds to about  $0.005\text{ }\gamma\text{ Re}$  per  $\text{cm}^2$  at this wave length). If only a few micrograms of rhenium are present, one extraction with 20 or 10 ml. of ether should be made to keep the volume small, and the standards treated similarly. If the standard series method is used, tubes having a cross-section of  $1\text{--}2\text{ cm}^2$  may be used with the smaller volumes of ether; less than  $0.5\text{ }\gamma$  of rhenium can then be determined.

#### B. INDIRECT DETERMINATION BY CATALYSIS OF REDUCTION OF SODIUM TELLURATE BY STANNOUS CHLORIDE

Perrhenic acid and its salts catalyze the reduction of sodium tellurate to elemental tellurium by stannous chloride.<sup>10</sup> Other things being the same,

<sup>10</sup> N. S. Poluektov, *J. Applied Chem. U.S.S.R.*, **14**, 702 (1941).

the amount of tellurium precipitated is proportional to the concentration of rhenium. If a protective colloid is added to the solution the tellurium remains in colloidal suspension and the concentration of rhenium can be obtained by determining the transmittancy of the suspension and comparing against a similar standard. By the procedure given below, 0.001 to 0.1  $\gamma$  of rhenium can be determined with an error of 10 to 20 per cent. Molybdenum interferes and must be separated if present in appreciable amounts. Nitric acid suppresses the reaction and other acids affect the degree of coloration, but the procedure following provides for the latter effect, the standards being prepared by addition of rhenium to the sample solution.

### Reagents

*Sodium tellurate*, 5 per cent aqueous solution.

*Tartaric acid*, 45 g. in 100 ml. of solution.

*Gelatin*, 0.5 per cent solution.

*Stannous chloride*, 100 g. tin dissolved in 250 ml. of hydrochloric acid.

*Perrhenic acid standard solutions*, containing for example 0.01 and 1  $\gamma$  Re per ml.

### Procedure

Transfer aliquots of the sample solution containing from 0.001 to 0.1  $\gamma$  Re to three graduated test tubes. To two of the tubes add standard perrhenic acid solution corresponding to 0.002–0.01 and 0.02–1  $\gamma$  of Re respectively. Dilute the solutions to 1.5 ml. and treat each (including a blank of 1.5 ml. of water) with 1 ml. of reaction mixture prepared by mixing 5 ml. of sodium tellurate, 2 ml. of tartaric acid, 1.5 ml. of gelatin, and 1.5 ml. of stannous chloride solutions. Mix and allow to stand for 1–2 hours, or until next day if no color is developed in the sample in this time. Obtain the extinction of the solutions at 430–470  $m\mu$ , comparing against the stronger standard if allowed to stand 1–2 hours or against the weaker if allowed to stand one day. Calculate the amount,  $x$ , of rhenium in the sample from the formula:

$$x = aE_x / (E_{a+x} - E_x),$$

where  $a$  = amount of Re added to one or the other of the two comparison solutions

$E_x$  = extinction of the sample solution

$E_{a+x}$  = extinction of the sample solution containing added Re.

If a photometer is not available, the suspensions may be compared by diluting the stronger to equal color intensity with the other with a mixture of 10 ml. reagent solution and 15 ml. of water.

### III. Applications of the Thiocyanate Method

#### A. DETERMINATION OF RHENIUM IN MOLYBDENITE

The concentration of rhenium in molybdenites varies from a few ten-thousandths of a per cent up to 0.01 per cent or rarely higher. Therefore separation of rhenium from most of the molybdenum must precede its determination. This separation may be effected by volatilization of rhenium heptoxide as already mentioned. The procedure given below is that described by Hiskey and Meloche<sup>11</sup> for the determination of rhenium in molybdenite. These authors avoid in large measure the difficulty caused by the presence of small amounts of molybdenum in the distillate by allowing the solution which has been treated with stannous chloride and thiocyanate to stand for a relatively long time before comparison until the color of the molybdenum thiocyanate complex has faded practically to zero. Ether is not used for extraction.

#### Apparatus

The distilling flask (300 ml.) must be provided with an inlet tube passing through a ground glass stopper nearly to the bottom of the flask; the exit tube is coiled for a distance of about 10 cm. to serve as an air-condenser, and is attached by means of a ground glass connection to a water condenser. A thermometer is suspended inside the flask.<sup>12</sup>

#### Procedure

Transfer 4 g. of pulverized molybdenite to a 250 ml. Erlenmeyer flask and add 20 ml. of concentrated nitric acid. After any initial frothing has ceased, add 5 ml. of fuming nitric acid and shake at intervals until vigorous reaction has subsided. Then heat the mixture just below the boiling point on a hot plate until red fumes have disappeared and carefully add 50 ml. of concentrated hydrochloric acid. Evaporate, with occasional replacement of the hydrochloric acid, until no more chlorine is evolved (usually 125–150 ml. of hydrochloric acid must be added). Reduce the volume to 25 ml. (do not allow to go to dryness), and cautiously add 75 ml. of concentrated sulfuric acid. Transfer the solution, together with any separated molybdic oxide, to the distilling flask. Distil at 260–270° while passing a mixture of two parts dry steam and one part air or carbon dioxide through the solution. Collect the distillate in a receiver immersed in an ice bath. Distil for 2½ hours at such a rate that 250 ml. of distillate are collected in that time.

Destroy any sulfur dioxide in the distillate by adding a few drops of

<sup>11</sup> C. F. Hiskey and V. W. Meloche, *Ind. Eng. Chem., Anal. Ed.*, **12**, 503 (1940).

<sup>12</sup> For an illustration of the distillation apparatus see L. C. Hurd and C. F. Hiskey, *Ind. Eng. Chem., Anal. Ed.*, **10**, 624 (1938).

strong aqueous bromine\* solution in an alkali bromide (add only enough to give a faint yellow color). To the distillate and three similar standard solutions containing 10, 50 and 100  $\gamma$  of rhenium, add 100 ml. of concentrated hydrochloric acid and (after cooling) 10 ml. of 20 per cent sodium thiocyanate solution, followed by 10 ml. of 20 per cent stannous chloride solution.<sup>13</sup> Allow the solutions to stand until the color of the molybdenum complex has faded out (30 or 45 minutes) and compare against the proper standard in 100 ml. Nessler tubes (vary the volume of one or the other of the solutions and measure the heights of the columns at the point of balance). Check the color intensities after 20–30 minutes to see whether the molybdenum color has faded completely from the sample solution.

TABLE 55

DETERMINATION OF RHENIUM IN THE PRESENCE OF MOLYBDENUM BY THE METHOD OF HISKEY AND MELOCHE<sup>14</sup>

(4 g. sample of  $\text{MoO}_3$  in each case)

Re added p.p.m.	Re found p.p.m.	Error p.p.m.
0.0	0.0	0.0
0.25	0.75	+0.5
1.0	1.5	+0.5
1.0	0.75	-0.25
2.5	3.25	+0.75
6.25	5.25	-1.0
13.75	13.25	-0.5
25.0	24.25	-0.75
10.0 <sup>a</sup>	11.75	+1.75

<sup>a</sup> 4 g. ammonium molybdate, 7.9 mg. Se.

Notes.—1. If the sample contains selenium, more or less of the latter will accompany rhenium into the distillate and be reduced to red colloidal selenium when stannous chloride is added. The selenium can be removed after the sample has been brought into solution by the following method. The solution is made at least 8 or 10 *N* with hydrochloric acid, 1 g. of sodium sulfite is added and the solution allowed to stand for 10–15 minutes. The solution is filtered, the precipitate washed, and the filtrate reduced to a volume of 25 ml. by slow evaporation. The determination is then continued in the regular way.

2. It seems possible that rhenium may be determined in the distillate by the method of Hoffman and Lundell after precipitation with hydrogen sulfide in the presence of arsenic (p. 375).

<sup>13</sup> Alternatively, take a 50 or 60 ml. aliquot of the 250 ml. distillate, transfer to a 100 ml. Nessler tube and add 20 ml. of hydrochloric acid, 2 ml. of thiocyanate and 2 ml. of stannous chloride solution.

<sup>14</sup> Representative data, C. F. Hiskey and V. W. Meloche, *Ind. Eng. Chem., Anal. Ed.*, **12**, 503 (1940).

B. DETERMINATION OF RHENIUM IN PYROLUSITE<sup>15</sup>

The concentration of rhenium in pyrolusite may attain a maximum of a few parts in ten million. The procedure for the determination of rhenium in this material will be briefly outlined. One hundred grams of pulverized pyrolusite are dissolved in warm hydrochloric acid, and insoluble material filtered off after diluting the solution to about 300 ml. The filtrate is treated with 20 per cent stannous chloride solution to reduce ferric iron and give a clear pink solution. Sufficient potassium thiocyanate is added to give a concentration of 0.6 g. per 100 ml., followed by enough stannous chloride to give 0.5 g. per 100 ml. After 5 minutes approximately 60 ml. of ethyl ether are added to the cold solution, and molybdenum and rhenium thiocyanates extracted. The extraction is repeated until the absence of any appreciable color in the ether layer shows that all the molybdenum and rhenium has been removed. The combined ether extracts are heated on a water bath at 70° C. until the volume has been reduced to 5 or 10 ml., and 15 ml. of 1:1 hydrochloric acid are then added. The remaining ether is evaporated by blowing air on the surface of the residue. Thirty per cent hydrogen peroxide is added dropwise until all brown, red or orange color disappears. The solution is allowed to stand for 15 minutes, with occasional addition of hydrogen peroxide to prevent the return of any color. The solution is diluted to 200 ml. with sulfuric acid (sp. gr. 1.8) and distilled as described on p. 381. The distillate should smell only faintly of sulfur dioxide. The separation of sulfur leads to low results. Bromine vapor is bubbled into the distillate to destroy the sulfur dioxide (faint yellow color). The colorimetric determination is made as already described (p. 382).

A similar procedure should be applicable to other minerals low in molybdenum. It is possible that the distillation of the mixture of the isolated rhenium and molybdenum can be omitted and the procedure of Hoffman and Lundell (p. 378) applied.

<sup>15</sup> L. C. Hurd and C. F. Hiskey, *Ind. Eng. Chem., Anal. Ed.*, **10**, 623 (1938).

## CHAPTER XXXVII

### RHODIUM

#### I. Separations

In the systematic analysis of the platinum group metals, osmium and ruthenium are first separated by volatilization of the tetroxides, and palladium, rhodium, and iridium are then precipitated as the hydrous oxides in the presence of bromate at a regulated acidity.<sup>1</sup> The hydrolytic precipitation of rhodium is complete at pH 6. A reprecipitation of the hydrous rhodium oxide is required to free it from platinum. Palladium is separated as the dimethylglyoxime compound, and rhodium is then precipitated as metal, and thus separated from iridium, by reduction with titanous chloride in hot sulfuric acid solution. The rhodium must be dissolved and reprecipitated to eliminate the small amount of iridium which has been carried down. No data are available to show how well these separations succeed when very small amounts of rhodium are associated with large amounts of the other metals of the group.

Hydrogen sulfide produces little precipitation of rhodium from a very dilute solution in sulfuric acid. Precipitation takes place more readily from hydrochloric acid solution but is not complete.

#### II. Determination with Stannous Chloride

By far the best color reaction for rhodium is that with stannous chloride, which when heated with a hydrochloric acid solution of rhodium (III) slowly produces a red color.<sup>2</sup> The color is brownish at first in solutions not too dilute, and passes into a reddish color on continued heating. The resulting solution turns yellow if diluted with relatively much water but remains red if diluted with 2 *N* hydrochloric acid. A satisfactory explanation of these color changes does not seem to have been advanced. The reaction is even more sensitive than the corresponding one with platinum, and may be used for the determination of very small quantities of rhodium.<sup>3</sup> The method has not been investigated systematically.

<sup>1</sup> R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

<sup>2</sup> Another color reaction deserves mention, namely the one with iodide. When a rhodium (III) solution is heated with potassium iodide (about 1 per cent) in the presence of hydrochloric acid (0.5 *N*) a brown color develops slowly. The reaction product is slightly soluble, a turbidity being produced when the rhodium concentration is as low as 1:100,000. This reaction can probably be used colorimetrically. The iodine liberated by air oxidation must be destroyed.

<sup>3</sup> V. N. Ivanov, *J. Russ. Phys. Chem. Soc.*, **49**, 601 (1910); W. Singleton, *Ind. Chemist*, **3**, 121 (1927).

The writer has obtained satisfactory results by the tentative method given below. Either the initial red color, or the yellow color obtained by dilution with water may be measured, the latter being more sensitive. If the yellow color is to be measured, the solution should preferably be allowed to stand for 1 hour after dilution, at the end of which time the color intensity is virtually constant. The concentration-extinction curve is of an unusual type (Fig. 56). The red and the yellow reaction products can be extracted with ethyl acetate if the aqueous solution contains a sufficiently high concentration ( $>2\text{ }N$ ) of hydrochloric acid. The organic solvent is colored yellow.

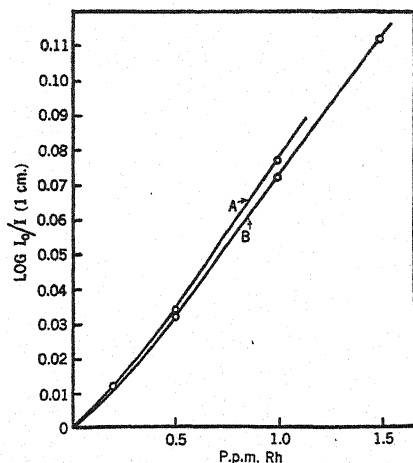


Fig. 56.—Determination of rhodium with stannous chloride. Five ml. of rhodium solution heated at  $100^{\circ}$  for 1 hour with 10 ml. of 10 per cent stannous chloride in  $2\text{ }N$  hydrochloric acid; then diluted to 50 ml. with water and transmittancy determined with blue filter (Jena BG-12) after 30 minutes (curve B) and after 1 hour (curve A)

The other platinum metals interfere by giving more or less strongly colored solutions under the conditions of the determination. The quantitative effect of iridium is of interest, since in the method of separation referred to in I the rhodium is finally left with this element, from which it is separated by precipitation with titanous chloride; some iridium is co-precipitated with the metallic rhodium. A solution containing  $50\text{ }\gamma$  of rhodium and approximately  $200\text{ }\gamma$  of iridium (IV) showed  $78\text{ }\gamma$  of rhodium when analyzed by the procedure given below, the yellow color obtained on dilution with water being measured. The error can possibly be reduced by measuring at a suitable wave length the transmittancy of the red solution of rhodium obtained by dilution with hydrochloric acid; iridium gives a brown solution after heating with stannous chloride.

### Special Solutions

*Stannous chloride*, 10 per cent solution of the dihydrate in 2 *N* hydrochloric acid.

*Standard rhodium solution*, 0.01 per cent. This may be prepared by fusing 10 mg. of finely divided rhodium metal with a gram or two of potassium pyrosulfate in a silica crucible until all the metal has been brought into solution, dissolving the melt in 1 *N* sulfuric acid, and diluting to 100 ml. with the same acid.

### ¶ Procedure

Transfer the neutral or only slightly acid sample solution (10 to 100  $\gamma$  of rhodium) to a test tube or a 1.8  $\times$  15 cm. flat-bottomed color comparison tube, dilute to 5.0 ml. with water, and add 10.0 ml. of stannous chloride solution. Mix and heat for 1 hour in a bath of boiling water. At the same time, treat in the same manner standard solutions for comparison or for construction of the reference curve. Cool to room temperature and dilute to 50 ml. in a volumetric flask with (a) 2 *N* hydrochloric acid, or (b) with water. If (a) is followed, the transmittancy of the red solution may be determined at once with the aid of a green or blue filter; if (b) is followed, allow the mixed solution to stand at room temperature for 1 hour before determining the extinction with a blue filter.

When very small amounts of rhodium are present, the solutions may advantageously be compared in the usual tubes (p. 42). As little as 1  $\gamma$  of rhodium will impart a faint pink tinge to a solution having a cross-section of 2 cm.<sup>2</sup>



## CHAPTER XXXVIII

### RUTHENIUM

#### I. Separations

It is likely that the macro method for the separation of ruthenium by volatilization of the tetroxide can be extended to traces, but no data are available. Briefly, the method is carried out as follows.<sup>1</sup> The solution from which osmium tetroxide has been distilled is evaporated to dryness on the steam bath, the residue is taken up in a little hydrochloric acid, and the liquid evaporated. The evaporation with hydrochloric acid is repeated until oxides of nitrogen are no longer evolved. The residue is dissolved in 1:3 sulfuric acid and the solution evaporated until sulfuric acid fumes appear.<sup>2</sup> The solution is transferred to a special distilling flask (p. 346) and diluted with water to give a solution containing approximately 10 per cent by volume of sulfuric acid. Ten per cent sodium bromate solution equal to the volume of the sample is added to the distilling flask, the solution is heated to boiling, and the distillation continued for one and one-half hours while a slow current of air is passed through the apparatus. The ruthenium tetroxide is absorbed in 1:1 hydrochloric acid saturated with sulfur dioxide. To assure the complete expulsion of ruthenium, more bromate (about one-fourth of the original amount) is added and the distillation is continued for one hour.

Isolation of ruthenium from the distillate can be effected by hydrolytic precipitation of hydrous ruthenium (III) oxide. The absorbing solution is first evaporated to a moist residue on the steam bath, a few milliliters of concentrated hydrochloric acid are added, and the covered beaker is heated on the steam bath for one-half hour. Water is added (about five times the volume of the acid) and boiled to bring all the ruthenium into solution.<sup>3</sup> Any silica in the solution may be filtered off at this point.

<sup>1</sup> R. Gilchrist, *Bur. Standards J. Research* **3**, 993 (1929); **12**, 283 (1934). R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

<sup>2</sup> The purpose of this treatment is to remove chloride which hinders the volatilization of ruthenium tetroxide. Ruthenium can be distilled directly from the solution from which osmium has been eliminated if sodium bromate and more nitric acid are added, but the minimum time for complete distillation of ruthenium (macro amounts) is then three and one-half hours. Elimination of hydrochloric acid before distillation has the added advantage of preventing the possible deposition of ruthenium dioxide on the walls of the distilling apparatus. Distillation of ruthenium tetroxide from alkaline solution in the presence of chlorine is not advisable because of possible loss of ruthenium by carrying down with the precipitated iridium hydroxide.

<sup>3</sup> This solution may perhaps be used for colorimetric determination without further treatment.

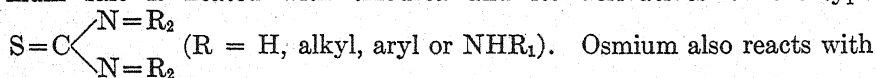
The solution is heated to boiling and treated with 10 per cent sodium bicarbonate until a precipitate forms (possibly a little aluminum may be added to give aluminum hydroxide to collect amounts of ruthenium too small to precipitate alone). Bromocresol purple indicator solution is added and the addition of bicarbonate continued until the indicator changes from yellow to blue (ruthenium is completely precipitated at pH 6). The solution is boiled for 5 minutes to coagulate the precipitate and filtered through an inorganic filter. The precipitate may be washed with 1 per cent ammonium sulfate and dissolved in dilute hydrochloric acid for the colorimetric determination of ruthenium (p. 389).

Solutions other than hydrochloric-sulfurous acid may be used to absorb ruthenium tetroxide. A 3 per cent solution of hydrogen peroxide (free from acetanilide) has been recommended for the purpose.<sup>4</sup> Ten milligrams of ruthenium distilled as described above from a volume of about 225 ml. could be quantitatively caught in two solutions of hydrogen peroxide having the respective volumes of 35 and 15 ml. The absorbing solutions must be cooled in ice. The hydrogen peroxide remaining after the absorption can be destroyed by adding a little hydrochloric acid (0.5 ml. per 100 ml. of solution) and boiling. This method would seem to have advantages for collecting ruthenium for colorimetric determination and should be studied further from this standpoint.

## II. Methods of Determination

### A. METHODS BASED ON THE USE OF THIOUREA AND DERIVATIVES

Strongly colored products are obtained when an acid solution of a ruthenium salt is heated with thiourea and its derivatives of the type



Osmium also reacts with some of these compounds. Various reagents of this type have been studied qualitatively by Steiger,<sup>5</sup> and his findings are partially summarized in Table 56.

Rubeanic acid also reacts with ruthenium (blue color, limit of detection 0.2  $\gamma$  Ru per ml.).<sup>6</sup>

The hue and the strength of the color given by thiourea with ruthenium depend markedly upon the acid concentration. In the acidity range 0.1 to 4 *N* (hydrochloric acid) the color varies from greenish to blue, the intensity being greater at the higher acidities. In 6 *N* hydrochloric acid a

<sup>4</sup> W. J. Rogers, F. E. Beamish, and D. S. Russell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 561 (1940). These authors precipitate ruthenium from the absorbing solution with thionalide.

<sup>5</sup> B. Steiger, *Mikrochemie*, **16**, 193 (1934-35).

<sup>6</sup> H. Wölbling and B. Steiger, *Mikrochemie*, **15**, 295 (1934).

violet color is obtained whose intensity is about the same as that of the blue color at 4 *N*. The reaction may conveniently be carried out at 2–4 *N* acidity, preferably the latter. The color develops rapidly on heating, and is moderately stable. Water may be used for diluting the acid solution to volume. The reaction product is apparently only slightly soluble. A solution containing 50  $\gamma$  of ruthenium in 10 ml. gives a slight turbidity on heating, but one containing 25  $\gamma$  in the same volume does not. Ferric iron produces a turbidity due to separation of sulfur.

Among the derivatives of thiourea, the writer has tried only phenylthiosemicarbazide for the determination of ruthenium. It gives a beautiful red or red-violet color in hot acid solution. The color intensity is much greater in 4 *N* hydrochloric acid than in 1 *N*. The sensitivity is greater than that of the thiourea reaction. The visual sensitivity amounts to

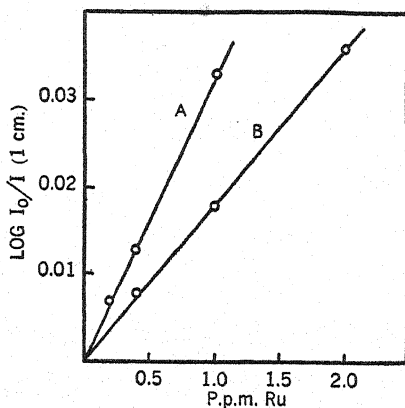


Fig. 57.—Determination of ruthenium with phenylthiosemicarbazide (A) and with thiourea (B).

about 0.5  $\gamma$  ruthenium per cm.<sup>2</sup> The colored compound can be extracted with butyl alcohol from the diluted acid solution, and 0.5  $\gamma$  of ruthenium will impart a color to 0.5 ml. of the alcohol. Ferric iron interferes by giving a turbidity and, if present in more than very small amounts, a red color. Practically, the effect of iron is not important since ruthenium will as a rule be isolated by distillation of the tetroxide before it is determined. Determinations of 5 and 10  $\gamma$  of ruthenium in the presence of 0.1 mg. of ferric iron yielded the values 7 and 11  $\gamma$  respectively. Reduction of ferric iron by stannous chloride is of limited value only, since the color given by ruthenium under these conditions is diminished in intensity.

### ¶ Procedure

To 10 ml. of sample solution 4 *N* in hydrochloric acid and containing up to 25  $\gamma$  of ruthenium, or more if thiourea is to be used as reagent, add either

TABLE 56  
COLORIMETRIC REAGENTS FOR RUTHENIUM

No.	Reagent	Color of product	Limit of detection Ru $\gamma$ /ml.
1	$\text{S} = \text{C} \begin{cases} \text{NH}_2 \\ \text{NHCH}_3 \end{cases}$	Blue	0.08
2	$\text{S} = \text{C} \begin{cases} \text{NH}_2 \\ \text{NHC}_2\text{H}_5 \end{cases}$	Blue	0.08
3	$\text{S} = \text{C} \begin{cases} \text{N}(\text{CH}_3)_2 \\ \text{NHCH}_3 \end{cases}$	Red	0.13
4	$\text{S} = \text{C} \begin{cases} \text{N}(\text{CH}_3)_2 \\ \text{N}(\text{CH}_3)_2 \end{cases}$	Violet	0.13
5	$\text{S} = \text{C} \begin{cases} \text{NHNH}_2 \\ \text{NH}_2 \end{cases}$	Red $\rightarrow$ green	0.14
6	$\text{S} = \text{C} \begin{cases} \text{NH}_2 \\ \text{NHNHC}_6\text{H}_5 \end{cases}$	Violet	—
7	$\text{S} = \text{C} \begin{cases} \text{NHNHC}_6\text{H}_5 \\ \text{NHC}_6\text{H}_5 \end{cases}$	Violet	0.025
8	$\text{S} = \text{C} \begin{cases} \text{NHC}_6\text{H}_5 \\ \text{N}-\text{C}_6\text{H}_5 \\   \\ \text{NH}_2 \end{cases}$	Violet	0.017
9	$\text{HS}-\text{C} \begin{cases} \text{NHC}_6\text{H}_5 \\ \text{N}-\text{NHC}_6\text{H}_5 \end{cases}$	Violet	0.025
10	$\text{S} = \text{C} \begin{cases} \text{NHNH}_2 \\ \text{NHNH}_2 \end{cases}$	Red	0.6
11	$\text{S} = \text{C} \begin{cases} \text{NH}-\text{NHC}_6\text{H}_5 \\ \text{NH}-\text{NHC}_6\text{H}_5 \end{cases}$	Violet	—

The ruthenium compounds of 5, 7, and 8 (and perhaps others) can be extracted with ether. Osmium reacts with 6, 7, 9, 11 (green colors) but not with 2, 3, 5.

0.5 ml. of freshly prepared 1 per cent alcoholic solution of phenylthiosemicarbazide or 0.5 ml. of 5 per cent aqueous thiourea solution. Heat in a bath of boiling water for 10 minutes, cool to room temperature, and dilute to 25 ml. or a smaller volume with water. Determine the transmittancy of the solution without undue delay, using a blue or green filter (phenylthiosemicarbazide as reagent) or a red one (thiourea as reagent).

### B. OTHER METHODS

Among the many other sensitive color reactions for ruthenium the following may be mentioned as possibly having value for quantitative application.

Ruthenium (III) in hydrochloric acid shows a strong brownish color. The color intensity is greatly dependent on the acid concentration, increasing with the latter. In 6 *N* hydrochloric acid the sensitivity is approximately 0.5  $\gamma$  ruthenium per  $\text{cm}^2$ . The chloro complex is not appreciably extracted from 1:1 hydrochloric acid by ethyl acetate.

Thiocyanate gives a pink color with low concentrations of ruthenium (III) in dilute acid solution. The color is stronger in dilute (0.2–1 *N*) hydrochloric acid than in stronger (4 *N*) acid. The sensitivity corresponds to 0.5  $\gamma$  or less of ruthenium per  $\text{cm}^2$  in 0.2 *N* hydrochloric acid. Phosphoric acid and fluoride diminish the color intensity or destroy the color, as does also stannous chloride. The colored compound can be extracted with butyl alcohol.

8-Hydroxyquinoline yields a green coloration with ruthenium (III) in acetate medium. The hydroxyquinolate can be extracted with chloroform.

An ammoniacal solution of ruthenium heated with sodium thiosulfate becomes pink.

## CHAPTER XXXIX

### SCANDIUM

The great difficulty in the practical colorimetric determination of scandium is the lack of suitable reactions for the separation of minute amounts of the element from its congeners.<sup>1</sup> The color and fluorescence reactions known at the present time are not specific and have only limited applicability.

A promising method for the determination of scandium in the absence of aluminum, beryllium, gallium, and some other metals reacting similarly involves the formation of a fluorescent complex with morin in neutral or faintly acid solution (p. 103). This reaction has been investigated only slightly from the quantitative standpoint. It appears that variation of the pH of the medium is of limited value in differentiating scandium from the other metals reacting with morin.<sup>2</sup> It is true that in strongly basic solution (sodium hydroxide) aluminum and gallium no longer fluoresce, but then beryllium gives an intense fluorescence. Scandium hydroxide precipitated in the presence of morin with sodium hydroxide shows fluorescence presumably because of the adsorbed morin. Magnesium hydroxide behaves in the same manner.

In connection with the use of morin it is of interest that certain salts or compounds of scandium with organic acids can be extracted from aqueous medium by such organic solvents as butyl alcohol, amyl alcohol, and ethyl acetate. The addition of an alcoholic solution of morin to the organic solvent phase produces a greenish fluorescence. In this way the concentration sensitivity of the morin reaction for scandium can be increased. This extraction method for the determination of scandium has been investigated in a preliminary way by S. E. J. Johnsen.<sup>3</sup> In his work, scandium was extracted as the thiocyanate or the benzoate. Unfortunately a number of elements, including ferric iron, aluminum, beryllium, gallium, and

<sup>1</sup> The slight solubility of scandium fluoride in the presence of hydrofluoric acid may find application in the separation of traces in conjunction with the use of a suitable collector (magnesium fluoride?). According to G. Beck, *Mikrochem. ver. Mikrochim. Acta*, **27**, 47 (1939), scandium alizarin-3-sulfonate is but slightly soluble in dilute acetic acid medium, and provides a method of separating scandium from the rare earths and aluminum; thorium accompanies scandium.

<sup>2</sup> G. Beck, *Mikrochim. Acta*, **2**, 9 (1937), states that scandium fluoresces best in dilute mineral acid solution, but we have been unable to observe any great difference in the effect of pH on the fluorescence of scandium and aluminum in the acid range.

<sup>3</sup> Unpublished work, University of Minnesota, 1942.

indium, are extracted under the same conditions as scandium, so that the extraction is valuable only as a means of concentration of scandium with consequent increase in sensitivity and not as a means of separation. Benzoate is preferable to thiocyanate in the extraction, since the interference of traces of iron is less with the former. Ferric iron in the organic solvent does not give a fluorescence when morin is added, but interferes by absorbing ultraviolet radiation. Aluminum, beryllium, gallium, and indium all fluoresce in the organic phase. The extraction of scandium is best made from a neutral or very slightly acid medium. Ammonium acetate may conveniently be used to buffer the solution to a  $pH$  of approximately 7. It is important that the sample and the comparison solutions have very nearly the same  $pH$  (a difference of 0.2 in  $pH$  will give rise to a large error). Under these conditions magnesium, zinc, and thorium give no fluorescence. Phosphate and fluoride hinder or prevent the extraction of scandium as well as of aluminum, beryllium, etc.

Johnsen gives the following directions for the determination of scandium by the extraction method in the absence of the interfering metals mentioned.

#### Reagents

*Ammonium acetate*, 50 g. in 100 ml. of water.

*Sodium benzoate*, 25 g. in 100 ml. of water.

*Morin*, 0.01 per cent in alcohol or acetone solution.

*Standard scandium solution*, 0.001 per cent Sc in 0.1  $N$  sulfuric acid.

#### Procedure

The sample solution may have a volume of 5 to 15 ml. and may contain from 0.2 to 5  $\gamma$  of scandium. If the solution is appreciably acid it should be brought to approximate neutrality with sodium hydroxide (free from aluminum). Treat the sample and standard solutions in 25 ml. glass-stoppered tubes as follows. Add 2.0 ml. of ammonium acetate and 1.0 ml. of sodium benzoate, mix, and add 2.0 ml. (or 3–4 ml. for quantities of scandium in the neighborhood of 5  $\gamma$ ) of ethyl acetate. Shake well and allow the phases to separate. Add 0.05 ml. of morin solution to the upper layer and mix by gentle agitation. Compare the fluorescence of the upper layers of the tubes in ultraviolet light.

## CHAPTER XL

### SILVER

#### I. Separations

In the absence of large amounts of metals giving sulfides insoluble in mineral acid medium, silver may be advantageously isolated by precipitation with hydrogen sulfide from a dilute sulfuric or nitric acid solution. The acidity of the solution may be in the neighborhood of 0.1 *N*. Chlorides and other halides should preferably be absent. Copper and mercury sulfides may be used as collectors. Copper need not be subsequently removed in either the rhodanine or cupric dithizonate methods if present to the extent of 0.5–1 mg. Mercury interferes in both methods and would have to be removed by gentle ignition of the precipitate. Since silver sulfide is one of the least soluble sulfides, it may be expected that the most minute amounts of silver can be isolated in this way under proper working conditions. The method should be applicable to such varied materials as silicates, meteorites, and biological substances. However, there are no data available to show the performance of the method when very minute quantities of silver are involved.

Extraction with dithizone in acid solution offers another possibility for the isolation of minute amounts of silver in the absence of gold, palladium, mercury, or much copper. Anions such as the halides and thiocyanate which form slightly soluble or complex silver salts must be absent. The value of the equilibrium constant of silver dithizonate is of such magnitude (p. 78) that small volumes of dithizone solution suffice to remove silver practically completely from fairly acid solutions. Silver may be separated in this way from moderate amounts of copper (*cf.* p. 399) but when the ratio Cu/Ag is very large the separation fails.

Another method of isolation which may be of use in colorimetric analysis, although primarily intended for the final determination of silver by cupellation, involves coprecipitation of silver with a precipitate of mercury-mercurous chloride produced by adding magnesium metal to a hydrochloric acid solution containing mercuric chloride, or coprecipitation with mercury-mercuric amino salt obtained by adding ammonia to a solution containing mercuric nitrate.<sup>1</sup>

Precipitation of silver as chloride, or better as bromide, with a slight excess of precipitant should be a useful method of separation in certain

<sup>1</sup> W. E. Caldwell and K. N. McLeod, *Ind. Eng. Chem., Anal. Ed.*, **9**, 530 (1937).



cases.<sup>2</sup> Mercurous bromide may be used as the gathering agent.<sup>3</sup> The mercury would have to be completely volatilized before the silver could be determined colorimetrically. An unpleasant feature of halide precipitation of silver is the necessity for the conversion of the precipitate into a soluble salt, which of course must precede the determination of silver by any colorimetric method.

## II. Methods of Determination

The most suitable reagents for the colorimetric determination of small amounts of silver are *p*-diethylaminobenzylidenerhodanine and dithizone. Neither reagent is specific for silver. Gold, palladium, and mercury will react with both under the conditions of the silver determination. Much higher acidities and neutral salt concentrations are permissible in the dithizone method than in the rhodanine method and moreover colored ions do not interfere in the former. Anions forming complex or slightly soluble salts with silver interfere seriously in both methods.

The possibility of the adsorption of silver by glassware must be borne in mind in the determination of small amounts of the metal. From a neutral solution silver is appreciably adsorbed by soft glass, only slightly by Pyrex, and not at all by fused silica. The adsorption is either much decreased or prevented if the silver solution is slightly acidified. If a silver solution must be concentrated by evaporation, a silica dish should be used. Very dilute standard silver solutions should be freshly prepared by dilution of a stronger stock solution.

### A. THE *p*-DIETHYLAMINO BENZYLIDENERHODANINE METHOD

This method for silver is applicable in the absence of palladium, gold, mercury, and cuprous copper which also give strongly colored products with the reagent. One drawback of the method is the necessity for close control of the acidity of the sample solution so that it is exactly the same as that of the comparison solution. A suitable acidity is 0.05 *N*. At higher acidities the sensitivity is strongly decreased. The color intensity depends upon the excess of reagent as well as upon the acidity.

The red-violet product given by silver with the rhodanine reagent is very slightly soluble and forms a stable, very finely divided, dispersion. When the silver concentration is in the neighborhood of 1 p.p.m. the maximum color is obtained practically at once after the addition of the reagent and

<sup>2</sup> E. E. Jelley, *J. Soc. Chem. Ind.*, **51**, 191T (1932), isolates silver as the bromide, dissolves the precipitate in ammonia, and determines silver in the solution with sodium dithionite (p. 403).

<sup>3</sup> Other possibilities are thallium (I) bromide and lead bromide, which in small amounts would not furnish enough metal to require removal of them before the determination of silver.

shows no significant change in the next half hour, but at lower concentrations (0.1–0.5 p.p.m.) the maximum intensity is not reached until after 15–20 minutes under the conditions recommended in the procedure below. Beer's law holds in the range 0.1 to 1 p.p.m. of silver (Fig. 58). Neutral salts may affect the color intensity.<sup>4</sup> Potassium nitrate in 1–2 per cent concentration changes the color strength only slightly, but 2 per cent of potassium sulfate was found to increase the extinction of a 0.4 p.p.m. solution of silver from the normal value of 0.047 to 0.070.

Lead and copper in small amounts are without great effect. Thus a solution containing 10.0  $\gamma$  of silver in 25 ml. yielded the value 9.2  $\gamma$  in the presence of 20 mg. of lead, and 9.8  $\gamma$  in the presence of 19 mg. of copper

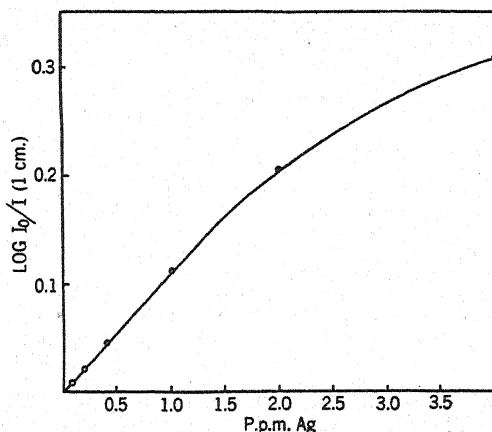


Fig. 58.—Determination of silver with diethylaminobenzylidenerhodanine (green filter). Acidity 0.05 *N* (nitric acid); 0.50 ml. 0.05% rhodanine reagent in a final volume of 25 ml. Extinctions represent constant values.

(as cupric sulfate) when the blue color due to the copper was compensated by the use of a similar reference solution.

#### Special Solutions

*p*-Diethylaminobenzylidenerhodanine, 0.05 per cent solution in ethyl alcohol. The methyl compound may also be used.

*Standard silver solution*, 0.01 or 0.001 per cent in 0.1 *N* nitric acid. Prepare by diluting a 0.100 per cent solution (0.158 g. of silver nitrate, dried at 110°, in 100 ml. of 0.1 *N* nitric acid solution).

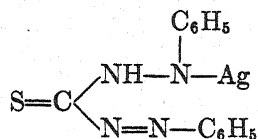
<sup>4</sup> According to I. C. Schoonover, *J. Research Natl. Bur. Standards*, **15**, 377 (1935), the general tendency of dissolved salts (calcium carbonate, sodium nitrate, potassium sulfate, etc.) is to increase the color intensity. Sulfuric acid in small amounts is also stated to increase the color strength.

## Procedure

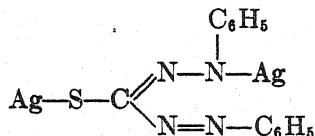
To 20 ml. of sample, 0.05 *N* in nitric acid, with a silver content of 0.1–2 p.p.m., add 0.50 ml. of rhodanine reagent, dilute to 25 ml. and mix. Determine the transmittancy of the dispersion (green filter) after 5 minutes for amounts of silver in the neighborhood of 1 p.p.m. or after 20 minutes with 0.1–0.5 p.p.m. The standards for the construction of the reference curve must have precisely the same acidity as the sample solution, and moreover should contain the same concentration of foreign salts as the sample.

### B. THE DITHIZONE METHOD<sup>5</sup>

Silver reacts quantitatively with dithizone even in 0.5 *N* mineral acid solution to yield the keto dithizonate



which dissolves in chloroform or carbon tetrachloride to give a yellow solution. In neutral or basic medium the enol compound



is formed, which is red-violet and virtually insoluble in carbon tetrachloride or chloroform. It is not important analytically, although it might find use as a separation form for silver.

Silver keto dithizonate is stable in the presence of alkalies, so that once formed it is not appreciably converted into the enol form, even when the carbon tetrachloride solution is shaken with 5 per cent sodium hydroxide solution. Therefore, after reaction of the silver with dithizone the excess of the latter can be removed from the carbon tetrachloride by shaking with dilute ammonia, and silver then determined colorimetrically by comparison against a standard solution of silver dithizonate. Beer's law holds.

Silver may be determined more expeditiously by the mixed color method (p. 399), especially if a photometer is available. If copper is absent, a dilute solution of dithizone may be used as reagent, and the mixed color varies from some shade of green to a yellow. The transmittancy of the solution may be determined with a yellow filter; a plot of  $\log 10 I/I_0$  gives almost or entirely a straight line, the values increasing with the silver content

<sup>5</sup> H. Fischer, G. Leopoldi, and H. von Uslar, *Z. anal. Chem.*, **101**, 1 (1935).

in accordance with the amount of dithizone converted into silver dithizonate (Fig. 59). Metals such as lead, zinc, etc. which react quantitatively with dithizone only in neutral or slightly basic medium do not interfere except when they are present in extremely high concentrations. The equilibrium constant for silver dithizonate has not been determined exactly but it appears to have a value of the order  $10^7$  (carbon tetrachloride), so that silver can be extracted quantitatively in 0.5–1 *N* acid solutions from which only minute traces of the metals mentioned are extracted unless excessive concentrations are present.

The extraction of silver is incomplete from the analytical standpoint when the solution is 6 *N* in sulfuric acid and only a slight excess of dithi-

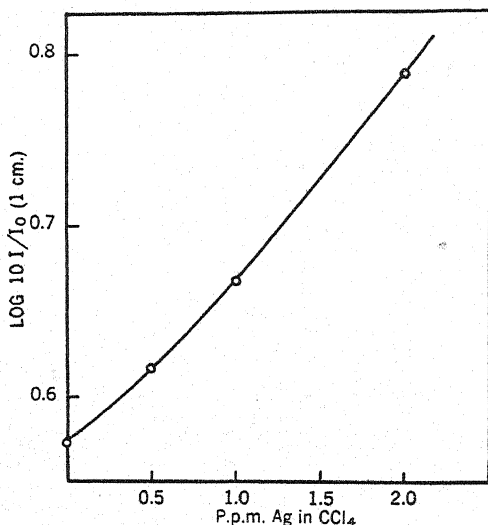


Fig. 59.—Determination of silver with dithizone by the mixed color method (yellow filter).

zone is present. Thus two 6 *N* sulfuric acid solutions containing respectively 10 and 15  $\gamma$  of silver yielded the values 9.5 and 13.9  $\gamma$  when analyzed according to the procedure given on p. 399 (10 ml. aqueous phase, 5 ml. dithizone).

In the presence of copper, silver can be determined by the mixed color method if cupric dithizonate is employed as reagent, the mixed color then ranging from violet to yellow. With a suitable yellow filter, a linear relation is found between  $10 I/I_0$  and the silver concentration in the carbon tetrachloride (Fig. 60). Moderate amounts of copper are nearly without effect, but as the quantity increases the values for silver show a negative error. The magnitude of the error is illustrated by the following figures

obtained in determining silver according to the procedure given below, the aqueous phase having a volume of 10 ml. (0.5 *N* in sulfuric acid) and the carbon tetrachloride a volume of 5 ml.:

Cu present mg.	Ag present mg.	Ag found mg.
10.0	0.010	0.0082
5.0	0.010	0.0091
2.5	0.010	0.0095

The mixed color method with copper dithizonate as reagent is recommended for general use. No special purification of acids, distilled water, etc. is required to remove traces of copper or other metals, as would be required in the dithizone mixed color method, and especially in the mono color method.

As already mentioned, silver can not be determined with dithizone when palladium, gold, and mercury are present because these metals have even a greater affinity than silver for dithizone.

### 1. The Mixed-Color Method

In the absence of copper a dilute solution of dithizone may be used as reagent, but otherwise a solution of cupric dithizonate must be used.

#### Special Solutions

*Dithizone*, 0.001 per cent (weight/volume) in analytical reagent carbon tetrachloride. Purification of the dithizone is not required, but the carbon tetrachloride should preferably be redistilled.

*Copper dithizonate*. Shake 0.001 per cent dithizone solution with a slight excess of dilute copper sulfate solution in about 0.05 *N* sulfuric acid for a minute or two, and then wash the carbon tetrachloride with 0.01 *N* sulfuric acid to remove suspended droplets of aqueous copper solution.

*Standard silver solution*, 0.001 per cent Ag in 0.1 *N* sulfuric or nitric acid (see p. 396).

#### Procedure

**With Dithizone as Reagent.**—Transfer 5–20 ml. of sample, approximately 0.5 *N* in sulfuric acid,<sup>6</sup> to a glass stoppered tube (1.8 × 15 cm. with flat bottom). Add 2.0 ml. of dithizone solution for 1 to 5  $\gamma$  of silver and correspondingly smaller or larger volumes for other quantities. Shake well for 15 seconds, allow the carbon tetrachloride to settle, and compare the hue of the latter with that of a series of standards obtained in the same way. Make the color comparison against a white background in good light. Alternatively, make the comparison by colorimetric titration, *i.e.*, add

<sup>6</sup> The solution may also be acidified with nitric acid (to not over 0.5 *N*) but the latter must be free from oxides of nitrogen which would oxidize dithizone and produce a yellow carbon tetrachloride solution resembling that of silver dithizonate.

standard silver nitrate solution to a comparison tube containing the same volume of dithizone and 0.5 *N* sulfuric acid solution as the unknown, with thorough shaking after each addition until the colors of the carbon tetrachloride layers match. The precision of the comparison is greatest when the solutions show the yellow-green color approximately midway between the colors of silver dithizonate and dithizone.

For amounts of silver greater than a few micrograms a photometer may be used to advantage. In this case shake the acidified silver solution in a separatory funnel with 10.0 ml. of dithizone solution (for as much as 25  $\gamma$  of silver) for about one-half minute, allow the carbon tetrachloride layer to settle and clarify, and deliver the liquid into the absorption cell through the dry stem of the funnel.<sup>7</sup> Obtain the transmittancy of the solution with the aid of an orange or yellow filter (Fig. 59). Construct the calibration curve by shaking 10.0 ml. of dithizone with acidified silver solutions of

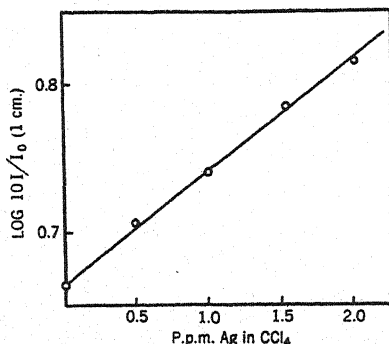


Fig. 60.—Determination of silver with cupric dithizonate (yellow filter).

various concentrations having approximately the same volume as the sample solution.

**With Cupric Dithizonate as Reagent.**—Transfer 5–20 ml. of sample, approximately 0.5 *N* in sulfuric acid, to a glass stoppered tube and add 2.0 ml. of copper dithizonate solution (for 0.5 to 5  $\gamma$  of silver). Shake for 2 minutes and compare the hue of the carbon tetrachloride with standards prepared similarly. Comparison may also be made by colorimetric titration.

If it is desired to use a photometer, transfer sufficient sample to contain 2–10  $\gamma$  of silver to a separatory funnel and shake for 2 minutes with 5.0 ml. of copper dithizonate solution. Use a yellow filter in obtaining the transmittancy of the solution (Fig. 60). The standard silver solutions

<sup>7</sup> Greater accuracy can of course be obtained by using 5 ml. of dithizone instead of 10, but then the amount of silver must not exceed 15  $\gamma$ .

for the construction of the reference curve should have about the same volume and acidity as the sample solution.

## 2. The Mono-Color Method

The following procedure<sup>8</sup> may be applied in the presence of the alkalis, alkaline earths, magnesium, aluminum, antimony, arsenic, and other metals which do not react with dithizone, as well as in the presence of such metals as lead, zinc, and cadmium which react only slightly or not at all in acid medium.

### Special Solutions

*Dithizone*, 5 mg. of purified reagent in 100 ml. of pure carbon tetrachloride.

*Ammonia wash solution*, 1:1000. The solution should impart no appreciable color to the carbon tetrachloride layer when shaken with dithizone solution.

### Procedure

The sample solution may conveniently contain 1 to 10  $\gamma$  of silver per milliliter. Acidify 10 ml. (or a similar volume) with 1 ml. of 4 *N* nitric or sulfuric acid, and shake thoroughly for 1-2 minutes with 5 ml. of dithizone in a small separatory funnel. Allow the two liquids to separate and draw off the carbon tetrachloride layer into another separatory funnel. Repeat the extraction with small portions of dithizone until the silver has been completely extracted, *i.e.*, until the last portion of dithizone remains an unchanged green after shaking for a minute or two. Finally wash the aqueous solution with a milliliter or two of carbon tetrachloride.

Wash the combined extracts once or twice with 5-10 ml. of 0.1 *N* sulfuric acid. (If metals reacting with dithizone in basic solution are present they must be completely washed out, otherwise they will of course react when the carbon tetrachloride solution is washed with ammonia in the next step.) Then shake the carbon tetrachloride solution with two 5 ml. portions of ammonia wash solution to remove excess dithizone. The last portion of wash solution must be colorless; if it is yellowish, wash further.

Dilute the silver dithizone solution to a definite volume with carbon tetrachloride and compare against a standard silver dithizonate solution similarly prepared from an appropriate volume of 0.001 per cent silver solution. It is permissible to separate droplets of the aqueous phase from the carbon tetrachloride prior to the color comparison by filtration of the latter through a small dry paper filter.

When a photometer is used, determine the transmittancy of the solution at 460  $m\mu$ .

<sup>8</sup> Taken from H. Fischer, G. Leopoldi, and H. von Uslar, *Z. anal. Chem.*, **101**, 1 (1935).

## C. THE CHLORIDE METHOD

The nephelometric determination of silver as the chloride lies beyond the scope of this book,<sup>9</sup> but a few words may be said about the turbidimetric

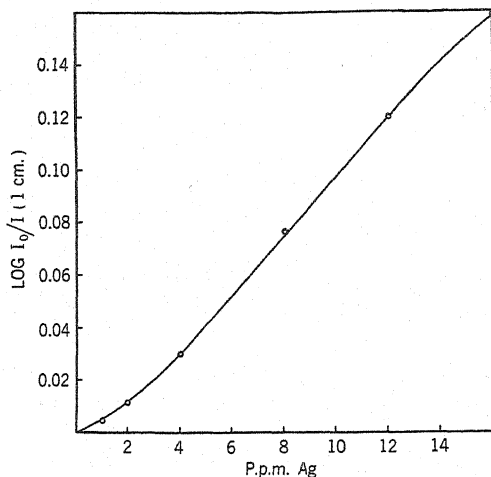


Fig. 61.—Turbidimetric determination of silver with chloride.

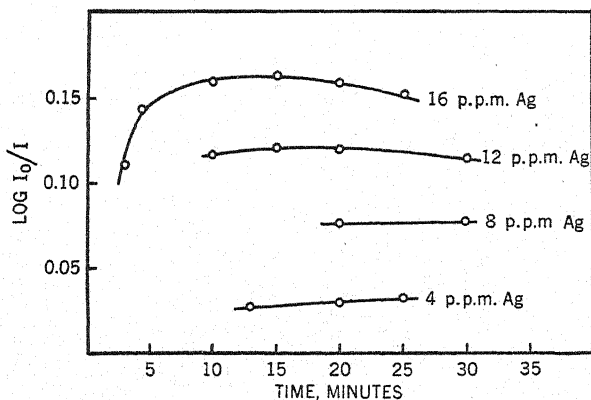


Fig. 62.—Variation of extinction with time in the turbidimetric determination of silver with chloride.

determination with the aid of a photometer. The relation between the concentration of silver and the extinction of the silver chloride suspension

<sup>9</sup> See A. B. Lamb, P. W. Carleton, and W. B. Meldrum, *J. Am. Chem. Soc.*, **42**, 253 (1920); J. M. Kolthoff and H. Yutzy, *J. Am. Chem. Soc.*, **55**, 1915 (1933); C. R. Johnson, *J. Phys. Chem.*, **35**, 540, 830, 2237, 2581 (1931); A. F. Scott and F. H. Hurley, *J. Am. Chem. Soc.*, **56**, 333 (1934); C. H. Greene, *J. Am. Chem. Soc.*, **56**, 1269 (1934).



is shown in Fig. 61. The suspensions were obtained by adding all at once 2.0 ml. of 0.05 *N* hydrochloric acid to 20 ml. of silver solution in 0.10 *N* nitric acid, which was swirled during the addition. The suspension was then made up to 25 ml. with water. The reproducibility of the suspensions prepared in this way was fairly good as shown by the following replicate figures for extinction: 0.004, 0.0045; 0.0105, 0.012; 0.030, 0.029, 0.030; 0.078, 0.077; 0.120, 0.122. The transmittancy of the suspensions was determined after 20 minutes (room temperature). In the case of the dilute suspensions, the amount of light transmitted decreases considerably after this time whereas it increases with more concentrated suspensions, so that this is an arbitrary period of standing (Fig. 62).

As well known, the opacity of silver chloride dispersions depends to a greater or less extent upon the amount and kind of foreign electrolytes present and this method cannot therefore be applied indiscriminately to solutions of unknown composition. The turbidimetric method is not very sensitive, the useful lower limit of the method being 1 p.p.m. of silver when a 1 cm. cell is used. The rhodanine method is twenty-five times as sensitive (p. 396, Fig. 58).

#### D. OTHER METHODS

In an ammoniacal solution containing gelatin, silver is reduced to the metal by sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) and a yellow sol is formed which is suitable for the determination of 1 to 20 p.p.m. of silver. A preliminary separation of silver from most metals is required.<sup>10</sup>

Silver may be determined photometrically as the sulfide by adding hydrogen sulfide water to an ammoniacal solution (as of separated silver chloride) and then acidifying to prevent the interference of such metals as iron and lead.<sup>11</sup>

2-Thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine gives a red to purple color (due to a slightly soluble compound) with silver in neutral or slightly acid solution.<sup>12</sup> This reaction has been applied to the determination of silver in very dilute solution.<sup>13</sup> This method is very similar to the rhodanine procedure, IIA above. The sensitivity of the two methods is of the same order and both are subject to the same interferences in general.

<sup>10</sup> E. E. Jelley, *J. Soc. Chem. Ind.*, **51**, 191T (1932). For the use of tannin as a reducing agent in the determination of silver see C. G. Makris and R. Menaché, *Ann. chim. anal. chim. appl.*, **22**, 117 (1940).

<sup>11</sup> P. W. Danckwortt, *Arch. Pharm.*, **252**, 29 (1914). T. V. Heidelberg, *Biochem. Z.*, **192**, 238 (1928).

<sup>12</sup> S. E. Sheppard and H. R. Brigham, *J. Am. Chem. Soc.*, **58**, 1046 (1936).

<sup>13</sup> J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.*, **14**, 148 (1942).

## CHAPTER XLI

### SODIUM

#### I. Separations

Since there are no salts of sodium markedly insoluble in aqueous medium, the separation of small amounts of the element must generally be accomplished by the precipitation of the major constituents of the sample with appropriate reagents. Potassium is perhaps best separated as the perchlorate, which is but slightly soluble in various organic solvents. When possible, the alkali salts are converted into perchlorates by evaporation to dryness with perchloric acid and the residue is extracted with ethyl acetate or other suitable solvent to dissolve sodium perchlorate and leave most of the potassium perchlorate. Less satisfactorily, potassium can be precipitated in alcoholic solution by evaporating the aqueous solution to a small volume and adding a saturated solution of ammonium perchlorate followed by sufficient ethyl alcohol to make its volume about 75 per cent in the mixture. These methods reduce the amount of potassium in solution to the point where sodium can be successfully determined by the method described below. Lithium can be separated from sodium by making use of the solubility of lithium chloride in organic solvents (*e.g.*, alcohol + ether, p. 301) in which sodium chloride is but slightly soluble. This method will fail if the amount of sodium chloride is very small.

Electrolysis with a mercury cathode is a useful method for removing large amounts of many heavy metals (*cf.* p. 115) preparatory to the determination of small amounts of sodium.

#### II. Determination by the Triple Acetate Method

The only procedure which comes into practical consideration for the determination of sodium is based on the insolubility of certain triple acetates of the composition  $\text{NaMe}^{\text{II}}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot \text{aq.}$  in an excess of the precipitating solution.  $\text{Me}^{\text{II}}$  may be magnesium, zinc, manganese, cobalt, and other metals. The use of zinc<sup>1</sup> and magnesium<sup>2</sup> uranyl acetates as precipitants in aqueous solution is most common. It is only by taking special measures that sodium can be quantitatively precipitated in this way. The reagent solution must be concentrated, and further must be saturated with the triple acetate at the same temperature that exists in the precipitation;

<sup>1</sup> H. H. Barber and I. M. Kolthoff, *J. Am. Chem. Soc.*, **50**, 1625 (1928); **51**, 3233 (1929).

<sup>2</sup> E. R. Caley and C. W. Foulk, *J. Am. Chem. Soc.*, **51**, 1664 (1929). E. Kahane, *Bull. soc. chim.*, **47**, 382 (1930); **53**, 555 (1933).

the sample solution must have a very small volume. Alcohol saturated with the triple acetate is used for washing. The precipitation is sometimes carried out in alcoholic solution, but this permits the presence of less potassium than when the precipitation is made in aqueous medium unless a double precipitation is made.<sup>3</sup> Potassium does not form a triple acetate but it may precipitate as potassium uranyl acetate when present in relatively high concentrations. Lithium must be absent because it may form a sparingly soluble triple acetate or will be coprecipitated with the sodium.

After the triple acetate has been quantitatively precipitated, collected, and washed, it may be dissolved in water and either uranyl ion or  $\text{Me}^{++}$  determined in the solution. Uranyl ion is fairly strongly colored and if the quantity of precipitate is not too small the absorption of the solution may be measured at a wave length of  $450 \text{ m}\mu$ .<sup>4</sup> The sensitivity with a suitable blue filter is approximately  $1 \gamma$  of sodium per  $\text{cm}^2$ . (p. 40) and Beer's law is followed if the light is sufficiently monochromatic. However it is usually more advantageous to add a reagent which will give a strong color with uranium. Hydrogen peroxide is very suitable for the purpose. In ammonium carbonate solution, it gives a yellow to orange color with uranyl ion.<sup>5</sup> The wave length of minimum transmission lies at  $460 \text{ m}\mu$  or less (it appears to depend upon the uranyl concentration). A wave length of  $520 \text{ m}\mu$  has been recommended by Arnold and Pray for the measurement of the transmittancy of the solution. Beer's law is followed over a considerable range of uranium concentration. The color intensity shows no appreciable change over a period of some hours.

It may be pointed out that determination of zinc (or magnesium) in the triple acetate precipitate should be advantageous in the determination of sodium in the presence of much potassium. The latter is partially precipitated as the double acetate when present in high concentrations, and therefore gives high results when uranyl is determined but presumably not if  $\text{Me}^{\text{II}}$  were determined. It has been proposed to use manganese uranyl acetate as a precipitant for sodium in order that the amount of precipitate may be found by oxidizing the manganese in it to permanganate.<sup>6</sup>

<sup>3</sup> For a thorough study of the determination of sodium with an alcoholic solution of magnesium uranyl acetate see F. Nydahl, *Ann. Agr. Coll. Sweden*, **6**, 37 (1937).

<sup>4</sup> L. Jendrassik and M. Holász, *Biochem. Z.*, **298**, 74 (1938); D. R. McCormick and W. E. Carlson, *Chemist-Analyst*, **31**, 15 (1942). The former authors dissolve the precipitate in a 20 per cent solution of sodium citrate. W. S. Hoffman, *Photometric Clinical Chemistry*. Morrow, New York, 1941; p. 174, states that the transmittancy of the solution of the triple salt in water varies markedly with temperature (3% per  $5^\circ \text{C}$ .) and therefore he dissolves it in  $0.1 \text{ N}$  ammonium thiocyanate in which the color is virtually independent of ordinary temperature variations.

<sup>5</sup> This reaction has been applied to the determination of sodium by E. A. Arnold and A. R. Pray, *Ind. Eng. Chem., Anal. Ed.*, **15**, 294 (1943).

<sup>6</sup> W. Woelfel, *J. Biol. Chem.*, **125**, 219 (1938); E. Leva, *ibid.*, **132**, 487 (1940).

The following procedure for the precipitation of sodium is that of Barber and Kolthoff (*loc. cit.*). Potassium may be present in fairly large amounts—as much as 10 mg. of potassium chloride with 0.5 mg. Na. Amounts of ammonium, calcium, barium, and strontium equal to some milligrams and perhaps even more may be present. Sulfate does no harm, but oxalate, tartrate, etc. should be absent. Phosphate in small quantity need not be removed before the precipitation. Any uranyl phosphate precipitated will remain undissolved when the triple acetate is finally dissolved in water and may be filtered off at that point. If much phosphate is present it can be precipitated with a slight excess of calcium hydroxide (use phenolphthalein as indicator).

See a recent paper by Broadfoot and Browning for the determination of sodium in plant material.<sup>7</sup> In the procedure (gravimetric) used by these authors the interference of large amounts of potassium is minimized by the addition of a regulated amount of nitric acid to the precipitant.

### Reagents

*Zinc uranyl acetate.* Mix equal volumes of solutions (a) and (b), allow to stand 24 hours at the temperature at which the precipitation is to be made and filter off the precipitate of sodium zinc uranyl acetate usually formed from traces of sodium in the reagents. If no precipitate appears add a little sodium chloride to saturate the solution with the triple acetate and filter. Keep the solution in a Pyrex bottle.

*Solution (a).* Mix 10 g. of  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , 6 ml. of 30 per cent acetic acid and 50 ml. of water, and warm to dissolve.

*Solution (b).* Mix 30 g. of  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , 3 ml. of 30 per cent acetic acid and 50 ml. of water and warm to dissolve.

*Ethyl alcohol saturated with sodium zinc uranyl acetate.* Shake 95 per cent alcohol at room temperature with excess triple acetate until saturated (ca. one-half hour) and filter. Prepare fresh every one or two days.

*Ether or acetone, reagent quality.*

*Ammonium carbonate, saturated solution in 2 N ammonium hydroxide.*

*Hydrogen peroxide, 3 per cent.* The solution should give no color with ammonium carbonate. It is best obtained by diluting the 30 per cent solution.

*Standard sodium solution, 0.05 per cent Na.* Prepare from sodium chloride ( $\text{NaCl}/\text{Na} = 2.54$ ).

### Procedure

The solution may conveniently contain 0.1 to 0.5 mg. of sodium in a volume not greater than 0.5 ml. If the precipitate is to be separated by filtration, a small Pyrex beaker (10–20 ml.) may be used as the precipitation vessel, but if the sample has previously been ashed in a small dish or crucible, this may be used for the precipitation after the residue has been brought into solution. The precipitate may also be formed in a centrifuge tube and separated by centrifugation. If necessary the precipitation vessel

<sup>7</sup> W. M. Broadfoot and G. M. Browning, *J. Assoc. Official Agr. Chem.*, **24**, 916 (1941).

should be immersed in a bath of water to keep the temperature of its contents within a degree or so of that at which the reagent solution was saturated with the triple salt.

Add 5 ml. of zinc uranyl acetate solution and allow to stand for 30 to 60 minutes while stirring at frequent intervals to insure complete precipitation of the sodium. Then, by the use of a filter stick (see p. 366) draw off the liquid and suck the precipitate dry. Wash once with 0.5 ml. portion of zinc uranyl acetate, suck as dry as possible, and then wash with similar small portions of alcohol saturated with the triple acetate until all of the reagent solution has been removed. Finally, wash once or twice with ether or acetone and allow to stand until the latter has evaporated.

Dissolve the precipitate in water, transfer the solution to a 50 ml. volumetric flask, add 5 ml. of ammonium carbonate solution followed by 5 ml. of hydrogen peroxide, and dilute to the mark with water. Obtain the transmittancy of the solution with the aid of a blue or green filter, or light of wave length 500-525  $m\mu$ . Construct the standard curve by carrying known amounts of sodium through the procedure in the same manner as the sample.

## CHAPTER XLII

### THALLIUM

#### I. Separations

There are many possible reactions for the isolation of thallium and its separation from other elements, but only a few have been studied with reference to micro amounts of thallium.

Thallium (I) can be extracted quantitatively from cyanide medium by dithizone in the pH range 9–12, the optimum pH being 11 for a carbon tetrachloride solution of the reagent according to H. Fischer. Lead, bismuth, and stannous tin accompany thallium in this separation. From most of the other elements thallium can be separated easily in this way. Relatively much zinc, mercury, and nickel (more than 0.1 g. in 50 ml.) are said to make the extraction of thallium incomplete,<sup>1</sup> Manganese tends to be carried through with the thallium, and a second extraction should be made after destruction of the dithizone in the first extract if much manganese is present.

Thallic chloride can be extracted with ether from a 6 N hydrochloric acid solution. A drawback of this method is the coextraction of ferric chloride. Ether extraction combined with dithizone extraction from cyanide solution should provide a separation of thallium from all other metals. Thallic bromide can be extracted with ether from a hydrobromic acid solution and thus separated from all metals except gold according to Wada and Ishii.<sup>2</sup>

Thionalide is a specific precipitant for thallium in a tartrate-cyanide solution containing sodium hydroxide (see p. 412).

In the case of materials not containing large amounts of heavy metals, precipitation of thallium as sulfide may be of value. Thallous sulfide (S.P. =  $10^{-24}$ ) is quantitatively precipitated in neutral or ammoniacal medium. Mercury, lead, and silver sulfides may be suggested as collectors.

The low solubilities of thallous chloroplatinate, iodide, chromate,<sup>3</sup> cobaltinitrite, and phosphotungstate may find use in the separation of small

<sup>1</sup> L. A. Haddock, *Analyst*, **60**, 394 (1935).

<sup>2</sup> I. Wada and R. Ishii, *Bull. Inst. Phys. Chem. Research Tokyo*, **13**, 264 (1934).

<sup>3</sup> F. Ensslin, *Metall u. Erz*, **37**, 171 (1940), makes use of the precipitation of thallium as chromate in its determination in refined zinc. After the separation of lead as sulfate, sulfosalicylic acid is added to the solution, followed by excess ammonia and chromate. For other uses of sulfosalicylic acid in the separation of thallium, see L. Moser and A. Brukl, *Monatsh.*, **47**, 709 (1926).

quantities of the element. Perhaps potassium or rubidium can be added to gather small amounts of thallium when chloroplatinate, cobaltinitrite or phosphotungstate are used as precipitants; barium chromate may be expected to be useful for collecting thallous chromate. Thallic hydroxide is very slightly soluble and may be precipitated with ammonium or sodium hydroxide in a suitable oxidizing environment. Ferric hydroxide or hydrated manganese dioxide may be used as coprecipitators.

Precipitation of metallic thallium with zinc in hydrochloric or sulfuric acid solution is of value in the separation of the element from large samples (50–100 g.) of sulfides such as pyrite or sphalerite which have been brought into solution by appropriate means and oxidizing agents removed. The precipitate must be filtered off rapidly and washing omitted. The thallium and other metals such as copper, cadmium and lead can then be dissolved and further separations made by the methods already mentioned.

TABLE 57  
SOLUBILITIES OF SOME THALLIUM SALTS

Compound	Solubility g./100 ml.
TlBr	0.042 (18° C.)
TlCl	0.21 (0°)
Tl <sub>2</sub> PtCl <sub>6</sub>	0.0064 (15°)
Tl <sub>2</sub> CrO <sub>4</sub>	0.03 (60°)
TlI	0.002 (0°)

## II. Methods of Determination

The colorimetric methods for thallium are indirect. The iodine method, A, is the one commonly used.

### A. THE IODINE METHOD

Thallic salts in acid solution are quantitatively reduced to thallous by iodide. The iodine liberated can be determined by extraction with an immiscible solvent such as carbon tetrachloride or disulfide, or by adding starch suspension, and measuring the transmittancies. Bromine water is a suitable reagent for oxidizing univalent thallium to trivalent in hydrochloric acid medium (not in sulfuric). The excess bromine is removed by boiling, which however must not be prolonged for fear of reduction of some of the trivalent thallium. The safest procedure involves removal of most of the excess by boiling and destruction of any small remainder by the addition of phenol.<sup>4</sup> Other oxidizing agents must of course be absent. Small

<sup>4</sup> L. A. Haddock, *Analyst*, **60**, 394 (1935).

amounts of ferric iron are made harmless by carrying out the reaction between thallic salt and iodide in a solution containing phosphate.

The following procedure includes directions for the isolation of thallium by ether extraction of thallic chloride,<sup>5</sup> or by dithizone extraction of a thal-  
lous solution according to Haddock (*loc. cit.*). Some results obtained in the dithizone extraction method, with final determination of thallium by the starch-iodine method, are given in Table 58.

#### Special Reagents

*Bromine reagent.* Dissolve 10 g. of sodium dihydrogen phosphate in a mixture of 90 ml. fresh bromine water and 10 ml. of concentrated hydrochloric acid.

*Starch-glycerin.* Make 1 g. of starch into a paste with 5 ml. of water and add the suspension slowly to 50 ml. of boiling water. Then add 50 ml. of glycerin and boil for 5 minutes.

TABLE 58  
DETERMINATION OF THALLIUM BY THE IODINE METHOD AFTER ISOLATION WITH  
DITHIZONE<sup>6</sup>

Foreign metal	Thallium present $\gamma$	Thallium found $\gamma$
Cu, 0.5 g.	100	100
Cu, 1.0 g.	60	63
Cu, 1.0 g.	20	21
Ag, 1.0 g.	30	28
Fe, 0.5 g.	40	43
Sb, 0.5 g.	25	27
Mg, 0.5 g. (double Dz extraction)	70	75
Sn, 0.5 g. (double Dz extraction)	30	32
Hg, 0.1 g.	50	47
Zn, 0.1 g.	90	85
Ni, 0.1 g.	80	76
NaCl, 5 g.	70	68

*Phenol solution,* 25 g. of phenol in 100 ml. of glacial acetic acid.

*Potassium iodide solution,* 0.2 per cent in water. This solution should be freshly prepared from iodate-free iodide.

*Ethyl ether,* analytical reagent, or *dithizone solution,* 0.1 per cent in chloroform.

*Hydrogen peroxide,* 30 per cent.

*Standard thallium solution.* Prepare a 0.01 or 0.1 per cent Tl stock solution in 1 N nitric acid from thal-  
lous nitrate ( $\text{TlNO}_3/\text{Tl} = 1.303$ ), and dilute this to 0.001 per cent. The latter solution should be prepared fresh at frequent intervals.

<sup>5</sup> P. A. Shaw, *Ind. Eng. Chem., Anal. Ed.*, **5**, 93 (1933). According to Shaw, 0.5 mg. of thallium can be determined to within  $\pm 0.01$ –0.02 mg. in the presence of 5 mg. of copper, lead, iron, arsenic, mercury, tungsten and molybdenum (the carbon disulfide extraction method was applied in the determination of the liberated iodine after ether extraction of thallic chloride).

<sup>6</sup> Data of Haddock, *Analyst*, **60**, 394 (1935).



## ¶ Procedure

**Isolation of Thallium.**<sup>7</sup>—(a) *By ether extraction.* The sample solution should be 6 *N* in hydrochloric acid and should have a volume as small as feasible (not over 50 ml.). Add 5 ml., or more if necessary, of freshly prepared chlorine water to oxidize thallium to the trivalent state. Shake for one minute in a separatory funnel with an equal volume of ethyl ether previously shaken with 6 *N* hydrochloric acid. Extract with two more portions of ether and combine the ether extracts. The latter may be washed with a little 6 *N* hydrochloric acid if the aqueous solution contained copper, bismuth, or other metal, which if not removed might interfere in the final determination. Evaporate the ether to dryness in a small Erlenmeyer flask, and add 1 ml. of water, a few drops of hydrochloric acid and 2 ml. of concentrated sulfuric acid. Heat to fumes of sulfuric acid and add nitric acid dropwise until any oxidizable substances are destroyed, and a colorless or light yellow solution remains.<sup>8</sup> Add 25 ml. of ammonium chloride (150 g. per liter), and evaporate to dryness (guard against spattering) to destroy nitrites.

(b) *By dithizone extraction.* To ca. 50 ml. of neutral sample solution containing thallium in the thallous state (reduce with sulfurous acid or hydroxylamine hydrochloride) add 0.5 g. of potassium cyanide and 0.5 g. of ammonium citrate (*cf.* p. 285). Extract with four 10–15 ml. portions of 0.1 per cent dithizone in chloroform. Wash the combined extracts with 20–50 ml. of 1:1000 ammonia, and shake the latter with a few milliliters of dithizone to recover any small amounts of thallium that may have gone into the ammoniacal solution. Evaporate the chloroform extracts to dryness in a 100 ml. Kjeldahl flask or a small Erlenmeyer. Add 1 ml. of concentrated sulfuric acid to the residue, heat, and add small amounts of 30 per cent hydrogen peroxide until all organic material has been destroyed.

<sup>7</sup> *Samples of organic origin* (toxicological material) may be decomposed as follows according to Shaw (*loc. cit.*). A finely-divided sample of suitable size is treated with sufficient 1:1 hydrochloric acid to give a fluid mass, the mixture is heated to boiling and small amounts of potassium chlorate are added until the organic material is largely destroyed (*cf.* p. 327). The cool mixture is filtered to remove undecomposed fatty particles and the filtrate evaporated until it darkens slightly. The cold solution is treated with enough chlorine water to discharge the darkening and leave a considerable excess. Thallic chloride is then extracted with ether according to (a) above.

If the dithizone extraction method is to be applied it is preferable to decompose an organic sample with sulfuric-nitric acid (or perchloric acid in conjunction with sulfuric or nitric acid). The acid mixture is diluted, nearly neutralized, and hydroxylamine hydrochloride added (*cf.* p. 325), followed by citrate and sufficient base to make the solution slightly alkaline. Cyanide is then added and the extraction with dithizone made as in (b).

<sup>8</sup> Hydrogen peroxide (30 per cent) may be used instead of nitric acid. The subsequent addition of ammonium chloride may then be omitted.

**Determination of Thallium.**—Add 20 ml. of water to the residue from (a) or (b) above, followed by 1 g. of ammonium chloride (if procedure b was used) and 25 ml. of the bromine reagent. Heat to boiling in a wide-mouthed flask and boil at such a rate that the solution becomes colorless in 3 minutes. Cool rapidly to 18° C., adjust the volume to about 35 ml., add 0.25 ml. of phenol solution; mix, and allow to stand for 3 minutes. Then add 5 ml. of freshly prepared 0.2 per cent potassium iodide and 1 ml. of starch-glycerin solution. Mix and allow to stand for 5 minutes at 18°. Then determine the transmittancy at about 600 m $\mu$ . The reference solution should contain iodide, starch-glycerin, etc. in the same concentration as the sample solution, in order that there may be no error from the liberation of iodine by air-oxidation. It should be prepared at the same time as the sample solution.

#### B. THE THIONALIDE METHOD<sup>9</sup>

In this method thallium is precipitated by thionalide in a tartrate cyanide solution containing sodium hydroxide (no other metal is precipitated by thionalide in this medium). The washed precipitate is dissolved in acid and treated with phosphomolybdotungstic acid. On warming, the latter is reduced and the amount of thallium is found from the intensity of the blue color.

##### Reagents

*Thionalide*, 5 per cent solution in acetone (freshly prepared).

*Potassium cyanide*, 10 per cent (freshly prepared).

*Sulfuric acid*, 1 N.

*Ethyl alcohol*, 95 per cent.

*Phosphotungstomolybdic acid*. Reflux for 2 hours in a flask with a ground glass joint, a mixture of 1 g. phosphomolybdic acid, 5 g. sodium tungstate, 5 ml. concentrated phosphoric acid, and 18 ml. of water.

*Formamide*.

##### ¶ Procedure

The sample solution may have a volume of 3 to 5 ml., and should be neutral or very weakly acidic. Add 0.5 ml. of 2 N sodium hydroxide solution and 0.5 ml. of potassium cyanide solution to the sample in a centrifuge tube. Precipitate the thallium with 5–6 drops of thionalide solution. Heat on the water bath at 90° for about 5 minutes, stirring constantly, to convert the precipitate to the crystalline form. Cool, centrifuge, and remove the supernatant liquid with the aid of a capillary tube. Wash three times with 3 ml. portions of acetone, being careful that the whole interior of the tube is rinsed, centrifuging each time.

<sup>9</sup> R. Berg, E. S. Fahrenkamp, and W. Roebling, *Mikrochemie (Molisch Festschrift)*, 44 (1936).

Dissolve the precipitate in two drops of sulfuric acid and 1 ml. of alcohol, heating gently if necessary. Transfer the solution to a color comparison tube and rinse the centrifuge tube with 1 ml. of warm alcohol and once or twice with 1 ml. of warm water. Depending upon the quantity of precipitate, add 1 to 3 drops of phosphotungstomolybdic acid and 1.5 to 2 ml. of formamide. Mix and allow to stand at 40° for 15 minutes. At the same time treat a series of standard thallium thionalate solutions, obtained in the same manner, with phosphotungstomolybdic acid. Dilute to volume and compare the unknown solution in a colorimeter with the standard having the closest color intensity.

**Notes.**—1. Berg and his coworkers prepare a series of artificial standards from mixtures of aqueous solutions of Chicago blue, naphthylamine black and a trace of India ink by matching against the color developed by known amount of thallium thionalate, and use these standards in the preliminary estimation of thallium in a sample with an accuracy of 20 per cent. For an exact determination a second portion of sample and a quantity of thallium equal to the estimated value are precipitated, phosphotungstomolybdic acid is reduced by the dissolved precipitates and the two solutions compared in a colorimeter.

2. Other metals precipitated by thionalide can be determined similarly to thallium, except that the precipitate is washed with hot water and dissolved in pyridine.

### C. OTHER METHODS

Thallium can be determined turbidimetrically or nephelometrically by adding phosphomolybdic acid solution (0.2 ml. of 5 per cent) to a 0.1 *N* nitric acid solution of a thallos salt (5 ml., containing 10–50  $\gamma$  of Tl).<sup>10</sup> A stable yellow sol of thallos phosphomolybdate is formed, whose transmittancy can be determined after 5 minutes. Among the metals not giving precipitates with the reagent may be mentioned lead, cadmium, bismuth, and mercury (II). Mercury (I) gives a faint precipitate which dissolves on the addition of sufficient nitric acid. Potassium and ammonium salts should be absent, since they yield slightly soluble phosphomolybdates.

In pure solution, thallium can be determined as the sulfide by the addition of excess sodium sulfide to give a brown sol. The color is produced also in the presence of cyanide, and in this respect thallium behaves the same as lead and bismuth.

<sup>10</sup> T. Pavelka and H. Morth, *Mikrochemie*, **11**, 30 (1932).

## CHAPTER XLIII

### TIN

#### I. Separations

Precipitation with hydrogen sulfide in acid solution is an important method for the separation and concentration of traces of tin in the presence of iron and other elements not precipitated under these conditions. The precipitation should be made in the presence of tartaric acid if the solution contains tungsten, vanadium, and titanium. From copper and the other elements of the copper sub-group, tin can be separated by the precipitation of these with sulfide in basic solution, but this method is open to objection on the score of coprecipitation of tin. Tin can be precipitated and separated from copper in acid solution by hydrogen sulfide if sufficient thiourea is present to bind copper in a complex.<sup>1</sup>

When the nature of the sample permits, precipitation with ammonium hydroxide may be used to isolate traces of tin; a little ferric iron should be added to furnish iron hydroxide to collect the tin. Precipitation of tin with cupferron may be of value at times. Ferric iron can be used as a collector.

Volatilization procedures are of importance in isolating small amounts of tin. Stannic chloride boils at 114° C. and stannic bromide at 202°. The volatilization of the former may be effected by leading dry hydrogen chloride through a hot (ca. 200°) solution in concentrated sulfuric acid.<sup>2</sup> Distillation of stannic bromide is described on p. 416; it may be made from a sulfuric or perchloric acid medium.<sup>3</sup>

For the separation of tin from iron in the ash of materials of organic origin by fusion with a mixture of sodium cyanide and sodium carbonate followed by acidification to give insoluble Prussian blue see a paper by Stone.<sup>4</sup>

<sup>1</sup> N. Strafford, *Mikrochim. Acta*, **2**, 309 (1937).

<sup>2</sup> F. Leutwein, *Z. anal. Chem.*, **120**, 233 (1940). P. Klinger, E. Stengel, and H. Wirtz, *Metall u. Erz*, **38**, 124 (1941), dissolve the sulfides of tin and other metals in sulfuric acid and distil stannic chloride at 130-140°.

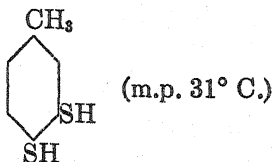
<sup>3</sup> See the Table on p. 31. Regarding the separation of tin from arsenic and antimony by the distillation method see H. Biltz and W. Biltz, *Ausführung quantitativer Analysen*. Hirzel, Leipzig, 1930; p. 329.

<sup>4</sup> I. Stone, *Ind. Eng. Chem., Anal. Ed.*, **13**, 791 (1941); B. Glassmann and S. Barsutskii, *Z. Untersuch. Lebensm.*, **56**, 208 (1928).

## II. Methods of Determination

### A. THE DITHIOL METHOD

In acid solution, toluene-3,4-dithiol



forms a magenta-red precipitate with stannous salts on warming.<sup>5</sup> Stannic tin also reacts, but more slowly than stannous. Thioglycolic (mercapto-acetic) acid may be used to reduce stannic tin to the stannous state. Many heavy metals react with the reagent to give more or less strongly colored precipitates. Bismuth gives a brick-red mercaptide; copper, nickel and cobalt give black precipitates, and silver, mercury, lead, cadmium, arsenic, etc. yield yellow precipitates.

The comparison of the unknown and standard suspensions must be made in reflected light according to Clark. If the tin content of the solution is kept below 30 p.p.m. it is not necessary to add a protective colloid (agar). Among the non-interfering substances (2 per cent solutions) may be mentioned the alkali and alkaline earth metals, magnesium, zinc, aluminum, the halides, cyanide, thiocyanate, borate, oxalate and tartrate. Fluoride delays the color development and phosphate decreases the color intensity. Iron has no effect up to 0.5 per cent, manganese none up to 1 per cent. Lead gives no color if the hydrochloric acid concentration is 7 per cent. Nitrites give a red color.

The reagent solution is not stable, being easily oxidized. The addition of thioglycolic acid increases its stability, but generally the reagent solution cannot be kept more than two weeks.

#### Special Solutions

*Toluene-3,4-dithiol.* Dissolve 0.2 g. of dithiol and 0.5 ml. of thioglycolic acid in 100 ml. of 1 per cent sodium hydroxide solution. Discard the solution when a white turbidity appears.

*Standard tin solutions.* (a) Dissolve 0.100 g. of tin in 10 ml. of concentrated hydrochloric acid, add 0.5 ml. of thioglycolic acid, and dilute to 100 ml. with water. (b) Dilute 10.0 ml. of solution (a) and 2 drops of thioglycolic acid to 100 ml. with water (1 ml. = 100  $\gamma$  Sn). Do not keep this solution longer than a day.

<sup>5</sup> R. E. D. Clark, *Analyst*, **61**, 242 (1936); **62**, 661 (1937). 4-Chloro-1,2-dimercaptobenzene may also be used as reagent.

### ¶ General Procedure

Transfer 5 ml. of slightly acid sample solution (containing not more than 10 p.p.m. Sn) to a color comparison tube (p. 42) and add 0.5 ml. of concentrated hydrochloric acid and 0.5 ml. of dithiol reagent. Prepare a suitable series of similar standards at the same time. Immerse the tubes in a boiling water bath for 30 seconds and then allow to stand for 1 minute. Compare the tubes by examining from the side in reflected light.

#### *Application of the Dithiol Method to the Determination of Tin in Foods*

Two methods for the determination of tin in food materials with the aid of dithiol have recently been described. In one of these tin is isolated by precipitation as the sulfide,<sup>6</sup> and in the other by volatilization as the bromide.<sup>7</sup> The following procedure gives directions for the latter method.

### ¶ Procedure

Incinerate 5 to 20 g. of sample in a silica dish.<sup>8</sup> Complete ashing is not necessary, nor even desirable for fear of formation of much stannic oxide. Transfer the charred mass to an all-glass distillation flask provided with a dropping funnel, a horizontal condenser, and a lead-in tube; the condenser should be connected to three small wash bottles for collecting the distillate. Rinse the dish with concentrated sulfuric acid and make up the volume in the distilling flask to 30 ml. Put the flask in an oil bath, raise the temperature to 220° C., and add hydrobromic acid (*sp. gr.* 1.46–1.49) from the dropping funnel at a rate of 1 or 2 drops per second while passing in a steady stream of dry carbon dioxide. After 30 to 45 minutes rinse the condenser and dilute the distillate to 50 or 100 ml. depending on the amount of tin expected.

Take an aliquot representing about 20  $\gamma$  of tin and add just enough phenol solution (25 per cent w/v in glacial acetic acid) to destroy the free bromine. Determine the acidity of the solution by titration with 1 *N* sodium hydroxide, using methyl orange as indicator. Take another aliquot, add phenol and a calculated amount of 30 per cent sodium hydroxide such that 0.5 ml. of concentrated hydrobromic acid remains in the solution. Then add 4 drops of thioglycolic acid (fresh 0.04 per cent aqueous solution),

<sup>6</sup> R. De Giacomi, *Analyst*, **65**, 216 (1940).

<sup>7</sup> N. H. Low, *Analyst*, **67**, 283 (1942). For a similar method for determining tin in biological materials see J. Schwaibold, W. Borchers and G. Nagel, *Biochem. Z.*, **306**, 113 (1940).

<sup>8</sup> The sample may be decomposed by wet digestion if desired, and this may in some instances be desirable if there is a possibility of the loss of tin by volatilization in the ignition procedure. De Giacomi (*loc. cit.*) uses 30 ml. of sulfuric acid and 10 g. of potassium sulfate for digestion of 10 g. of food sample.

3-4 drops of fairly stiff agar mucilage, and 1 ml. of dithiol reagent (0.1 per cent in 1 per cent sodium hydroxide). Dilute to 10 ml., heat in a boiling water bath for 1 minute, and compare against standards obtained in a similar manner from fresh tin solution (p. 416).

**Notes.**—1. No tin distills over at 200°. At least 30 minutes is required for the distillation.

2. At least twice as much arsenic as tin must be present to produce an interfering color tint. Boron does not interfere.

3. The accuracy of the procedure may be judged from the following figures (data of Low) obtained on 10-20 g. of various food materials:

Sn present, mg.....	0.40	0.10	0.66	0	0
Sn added, mg.....	0.50	0.50	0.50	0.50	0.50
Sn found, mg.....	0.90	0.60	1.14	0.50	0.50

### B. THE PHOSPHOMOLYBDIC ACID METHOD<sup>9</sup>

Stannous tin, in common with other strong reducing agents, reduces phosphomolybdic acid to molybdenum blue, which can be extracted with amyl alcohol. The colored compound is quite stable in amyl alcohol solution in the presence of air. A relatively large excess of phosphomolybdic acid is required to give the maximum color intensity. The law of Beer is obeyed. Tin may be reduced to the stannous state by aluminum in acid solution in a carbon dioxide atmosphere.

Copper and titanium are stated to be the only common metals giving the same reaction as tin under the conditions of the determination. Platinum, silver, mercury, lead, arsenic, antimony, bismuth, zinc, cadmium, nickel, cobalt, iron, and chromium do not interfere according to Strafford.

#### Special Solutions

*Phosphomolybdate reagent.* Solution A. Dissolve 2.5 g. of molybdic acid in 50 ml. of 1 *N* sodium hydroxide and dilute to 100 ml. with 2 *N* sulfuric acid. Solution B. Dissolve 0.44 g. of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  in 100 ml. of water.

Shortly before use prepare the mixed reagent by mixing 10 ml. of solution A and 4 ml. of solution B, and diluting to 200 ml. with water.

*Standard tin solution.* 0.010 per cent Sn in 1:20 hydrochloric acid. This solution should be prepared fresh each day by dilution of a stronger (e.g. 0.1 per cent) stannous solution.

#### ¶ Procedure

If the sample is of organic origin, decompose 5 g. (for < 50 p.p.m. tin) with sulfuric and nitric acids according to the procedure on p. 278. Dilute the clear solution to about 100 ml. with water and add 5 g. of thiourea

<sup>9</sup> N. Strafford, *Mikrochim. Acta*, **2**, 306 (1937).

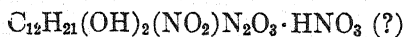
and also 2 g. of tartaric acid if appreciable amounts of titanium are present. Then add ammonium hydroxide until the solution is only slightly acid (pH 2-3, congo red paper). Cool, and saturate the solution with hydrogen sulfide. Heat on the steam bath for one-half hour and allow to stand for another half-hour. Filter through paper and wash three times with 10 ml. of hydrogen sulfide water. Transfer the paper and precipitate to a 100 ml. Kjeldahl flask, wash the precipitation vessel with 20 ml. of hot 1:1 nitric acid and add the latter to the flask. Add 1 ml. of concentrated sulfuric acid to the flask and digest the mixture. When oxidation appears complete add a little 30 per cent hydrogen peroxide. Then add 10 ml. of water to the cold mixture and evaporate to fuming.

Transfer the residue with the aid of 25 ml. 1:1 hydrochloric acid to a wide test tube ( $3.5 \times 18$  cm.) provided with a rubber stopper through which pass the stem of a 50 ml. funnel with stopcock and two tubes, also with stopcocks, for ingress and egress of carbon dioxide; the inlet tube should reach nearly to the surface of the solution, and the other should end at the bottom of the stopper. Drop 0.1 g. of aluminum foil into the tube, insert the stopper, and pass a fairly rapid current of carbon dioxide through the apparatus while gently heating. When the reaction subsides, raise the solution to boiling, close the stopcock of the exit tube, and cool in an ice bath. Then open the stopcock of the exit tube and allow 15 ml. of mixed phosphomolybdate reagent to run into the tube from the funnel. Close the exit tube stopcock and mix the contents of the tube by gentle shaking. After 5 minutes introduce 9.0 ml. of amyl alcohol and shake well to extract the molybdenum blue. In all of these operations an atmosphere of carbon dioxide must be maintained in the tube.

Dissemble the apparatus and pour the contents of the tube into a small separatory funnel. Reject the lower aqueous phase and run the amyl alcohol into a 10 ml. volumetric flask, add 1 ml. of ethyl alcohol for clarification, and adjust the volume to 10 ml. Determine the transmittancy of the solution with the aid of a red filter. Construct the reference curve by carrying known amounts (0.02-0.25 mg.) of tin through the procedure.

### C. OTHER METHODS

Cacotheline, a nitro derivative of brucine,



gives a violet color with an acid solution of stannous tin and other strong reducing agents such as antimony (III), titanium (III), uranium (III), rhenium (III), columbium (III), molybdenum and tungsten in lower valence states, sulfite, and thiosulfate. According to Strafford the color fades rapidly and the reaction is not suitable for quantitative purposes.



$\alpha$ -Dinitrodiphenylamine sulfoxide<sup>10</sup> has been used for the colorimetric determination of tin but has little to recommend it.

A semiquantitative method for the determination of small amounts of tin (IV) with anthraquinone-1-azo-4-dimethylaniline has been described.<sup>11</sup>

Quinalizarin gives a pink lake with stannic tin in weakly acid solutions. The reaction is not very sensitive. At pH 4.75 (acetate buffer) approximately 2  $\gamma$  of tin can be detected in 10 ml. of solution (1.8  $\times$  15 cm. tube). At a lower pH the sensitivity is less. The color develops slowly and an hour or more should be allowed for the attainment of full color intensity. Many metals react with quinalizarin in weakly acid medium, but since tin is readily separated by volatilization the reaction may prove of some value.

<sup>10</sup> G. S. Buchanan and S. B. Schryver, *Analyst*, **34**, 121 (1909).

<sup>11</sup> V. I. Kuznetsov and I. M. Bender, *J. Applied Chem. U. S. S. R.*, **13**, 1724 (1940); V. I. Kuznetsov, *ibid.*, **13**, 769 (1940).

## CHAPTER XLIV

### TITANIUM

#### I. Separations

The separation of titanium from vanadium, molybdenum, and phosphorus can be effected by double precipitation of titanium hydroxide with hot 1 *N* sodium hydroxide solution. The precipitation of titanium is not quite complete if iron is absent, but is quantitative when a little iron is present.<sup>1</sup> Titanium can also be separated from chromium in this way if the latter is first oxidized to the sexivalent state, as for example by the use of persulfate in sulfuric acid solution. Fusion with sodium carbonate and leaching of the melt with water serves the same purpose as the sodium hydroxide precipitation; if relatively much chromium is present, a little sodium nitrate should be used with the sodium carbonate.

Separation of titanium from iron can be made by double precipitation of ferrous sulfide in ammoniacal medium in the presence of tartrate. Extraction of ferric chloride with ether from a 1:1 hydrochloric acid solution is a good method of separating most of the iron from titanium.

Occasionally precipitation of titanium with cupferron can be put to good use in the isolation of the element (*cf.* p. 425). A little iron (III) or zirconium may be used as a collector. Titanium may thus be separated from nickel, cobalt, chromium, uranium (VI), and phosphorus but not from vanadium.

*p*-Hydroxyphenylarsonic acid,<sup>2</sup> which yields slightly soluble salts with titanium and zirconium in dilute mineral acid medium, may perhaps be found useful in isolating small amounts of titanium and separating it from iron, vanadium, molybdenum, etc.

#### II. Methods of Determination

##### A. THE HYDROGEN PEROXIDE METHOD

The yellow color produced when hydrogen peroxide is added to an acid titanium (IV) solution has long been utilized for the determination of the element.<sup>3</sup> The colored substance formed in the reaction is probably  $\text{TiO}_2(\text{SO}_4)_2$  or a similar ion.<sup>4</sup> The determination is usually carried out in a

<sup>1</sup> W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*. Wiley, New York, 1929; p. 455.

<sup>2</sup> C. T. Simpson and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.*, **10**, 642 (1938).

<sup>3</sup> A. Weller, *Ber.*, **15**, 2592 (1882).

<sup>4</sup> R. Schwartz, *Z. anorg. allgem. Chem.*, **210**, 303 (1933).

sulfuric acid solution having a concentration ranging from about 1.5 to 3.5 *N*. The titanium color is slightly weaker in 6 *N* sulfuric acid than in 1.5–2 *N* acid.<sup>5</sup>

A number of substances reduce the color intensity of peroxidized titanium solutions. Alkali metal sulfates show a slight bleaching effect (Table 59), which is stronger the lower the concentration of sulfuric acid in the solution.<sup>6</sup> In the presence of relatively much alkali sulfate the solution should contain 10 per cent by volume of sulfuric acid rather than the usual 5 per cent, and the standard should have the same acidity and preferably should contain about the same concentration of salt. Phosphate and

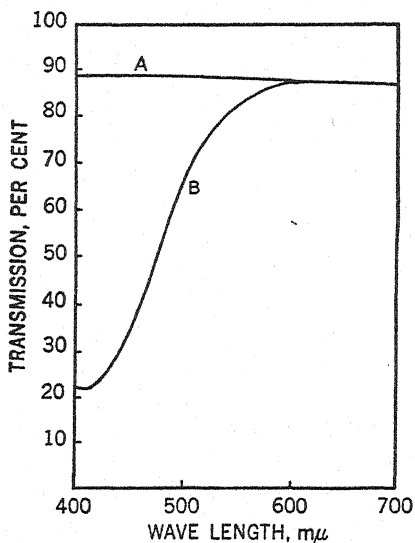


Fig. 63.—Transmission curves of peroxidized titanium solution containing 8 p.p.m. Ti (B) and blank solution (A) in 5.3 cm. long quartz cell (Michaelson and Liebhafsky, *Gen. Elec. Rev.*, **39**, 445 (1936)).

especially fluoride form complexes with titanium and seriously reduce the color intensity. Citric acid bleaches the color, but tartaric acid has practically no effect.

Iron interferes to a considerable extent because of its color. The color due to iron can be largely destroyed by the addition of phosphoric acid, which is added in like amount to the standard.<sup>7</sup> Vanadium and molyb-

<sup>5</sup> A solution containing 0.50 mg. Ti in 50 ml. of 6 *N* sulfuric acid was found to show the same color intensity as a solution of 0.47 mg. Ti in 50 ml. of 1.8 *N* acid.

<sup>6</sup> H. E. Merwin, *Am. J. Sci.*, **28**, 119 (1909).

<sup>7</sup> By the use of a green filter in the color comparison the error due to iron is largely eliminated but the titanium sensitivity is greatly reduced. (M. Bendig and H. Hirschmüller, *Z. anal. Chem.*, **92**, 1 (1933)).

denum also give yellow colors with peroxide; chromium (VI) gives an evanescent blue. The color given by vanadium is comparable in intensity to that given by titanium (Table 59) but the molybdenum color is much weaker. When a photometer is used, the effect of iron, nickel, chromium

TABLE 59

DETERMINATION OF TITANIUM BY THE PEROXIDE METHOD: THE EFFECT OF SOME FOREIGN SUBSTANCES

0.50 mg. titanium taken in each case; final volume 50 ml., containing 15 ml. 6 N sulfuric acid and 5 ml. 3 per cent hydrogen peroxide.

Foreign substance	Ti found mg.
1.0 g. $K_2SO_4$	0.48
1.0 ml. 85% $H_3PO_4$	0.39
2.0 mg. NaF	0.40
1.0 g. tartaric acid	0.49
0.050 g. $Fe^{III}$	0.66
0.25 mg. $V^V$	0.61
2.5 mg. $Mo^{VI}$	0.56

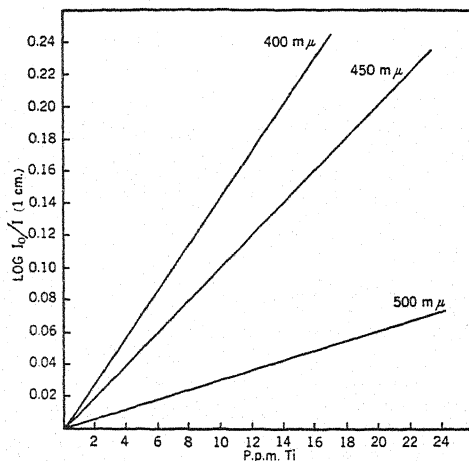


Fig. 64.—Extinction of peroxidized titanium solutions at 400, 450 and 500  $m\mu$ .  
(From data of Michaelson and Liebhafsky).

(III), and other colored ions not reacting with peroxide may be compensated by using a solution of the sample, not treated with peroxide, in the comparison cell.

The color intensity of peroxidized titanium solutions increases slightly with a rise in temperature. The solutions show very little change with

the passage of time. Beer's law holds for titanium concentrations as high as 50 p.p.m.<sup>8</sup>

#### Standard Titanium Solution

(a) *Preparation from potassium titanium oxalate.*<sup>9</sup> Weigh 3.68 g. of recrystallized and air-dried  $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  into a 500 ml. Kjeldahl flask, and add 8 g. of ammonium sulfate and 100 ml. of sulfuric acid. Gradually heat to boiling and boil for 5-10 minutes. Cool and pour the solution into 700-800 ml. of water. After cooling, dilute to 1000 ml. If the salt weighed out is pure and contains the proper amount of water, each milliliter of solution will contain 0.50 mg. of Ti. If it is not certain that these conditions are fulfilled, the solution should be standardized by precipitating the titanium with ammonia or preferably cupferron and igniting the precipitate to  $\text{TiO}_2$ .

To prepare a solution containing 0.50 mg.  $\text{TiO}_2$  per ml. weigh out 2.21 g. of  $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  and proceed as above.

(b) *Preparation from potassium fluotitanate.* Transfer 2.70 g. recrystallized and air-dried  $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$  to a platinum dish, add 100 ml. of 1:1 sulfuric acid, heat until strong fumes are evolved, cool, carefully rinse down the sides of the dish with water and again heat to strong fuming. To be certain that all of the hydrofluoric acid has been expelled, it is advisable to heat to fuming for a third time after rinsing down the sides of the dish. Pour the cold solution into 700-800 ml. of water, add 50 ml. of concentrated sulfuric acid, and dilute to 1000 ml. after cooling. Each milliliter of the solution should contain 0.50 mg. of Ti if the salt is pure and contains the proper amount of water. The strength of the solution may be checked by precipitating the titanium with ammonia or cupferron and igniting the precipitate to  $\text{TiO}_2$ .

To prepare a solution containing 0.50 mg.  $\text{TiO}_2$  per ml., weigh out 1.62 g. of  $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$  and proceed as above.

#### Procedure

Add 15 ml. of 6 *N* sulfuric acid to the sample solution (the final acidity may vary from 1.5 to 3.5 *N*) and, if iron is present in appreciable amounts, add dilute phosphoric acid from a buret or graduated pipet until the yellow color of ferric iron is destroyed. The same amount of phosphoric acid must be added to the standards. If the sample contains much sodium or potassium sulfate, add a like amount to the standards. Add 5 ml. of 3 per cent hydrogen peroxide and dilute the solution to 50 ml. in a volumetric flask.<sup>10</sup> Determine the transmittancy of the solution with the aid of a blue filter (maximum transmission at 420-430  $m\mu$ ).

For the determination of very small amounts of titanium, the standard series method, or better the colorimetric titration technique (p. 43) is to be preferred. In a 1.8  $\times$  15 cm. tube (internal cross section about 2  $\text{cm}^2$ .) 2  $\gamma$  of titanium shows a faint color easily distinguishable from a blank.

<sup>8</sup> H. Ginsberg, *Z. anorg. allgem. Chem.*, **211**, 401 (1933).

<sup>9</sup> W. M. Thornton, Jr. and R. Roseman, *Am. J. Sci.*, **20**, 14 (1930).

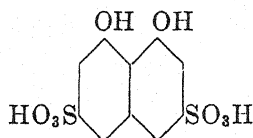
<sup>10</sup> The final concentration of titanium may conveniently be 2-25 p.p.m. if a photometer is used (1 cm. cell). A similar range of concentrations is suitable for comparison with a Duboscq type colorimeter.

## B. OTHER METHODS

Thymol gives a reddish yellow color with titanium in concentrated sulfuric acid solution.<sup>11</sup> The reaction is more sensitive than the one with hydrogen peroxide. The reagent is prepared by dissolving 5 g. of thymol in 5 ml. of acetic acid and diluting to 100 ml. with concentrated sulfuric acid. The solution of titanium in concentrated sulfuric acid is treated with 20 ml. of the reagent, diluted to 100 ml. with sulfuric acid, and compared against a standard similarly prepared. Both solutions must be at the same temperature; the color intensity decreases with a rise in temperature. When the sulfuric acid content of the solution is less than 80 per cent the color intensity is markedly decreased. Tungsten interferes.

Gallic acid produces a yellow to red-brown color in titanium solutions, particularly in the presence of acetate.<sup>12</sup> Salicylic acid has been used for the colorimetric determination of titanium.<sup>13</sup>

Chromotropic acid



(or its sodium salt) gives a brown color with titanium in acid solution, and has been employed for the determination of titanium.<sup>14</sup>

## III. Applications

## A. SILICATE ROCKS

Ordinarily in a rock analysis, titanium is determined in the solution remaining after titration of total iron by permanganate. The following procedure may be used for the determination in a separate sample.

## ¶ Procedure

Weigh 0.3 g. of rock powder into a platinum crucible, mix with 1.5 g. of anhydrous sodium carbonate and fuse in the usual way. Leach the melt with about 50 ml. of water on the steam bath; add a few drops of alcohol to reduce manganate. Filter through a small paper, keeping as much as possible of the residue in the beaker. Wash with water and discard the

<sup>11</sup> V. Lenher and W. G. Crawford, *J. Am. Chem. Soc.*, **35**, 141 (1913).

<sup>12</sup> P. N. Das-Gupta, *J. Indian Chem. Soc.*, **6**, 855 (1929). Catechol reacts with titanium in weakly acidic solution to yield an orange-red color (J. Piccard, *Ber.*, **42**, 4343 (1909)). The reaction is more sensitive than the one with hydrogen peroxide, but iron and other metals also give a coloration.

<sup>13</sup> J. H. Muller, *J. Am. Chem. Soc.*, **33**, 1506 (1911).

<sup>14</sup> P. Klinger, E. Stengel and H. Wirtz, *Metall u. Erz*, **38**, 124 (1941).

filtrate and washings. Dissolve the insoluble material in 50 ml. of 1:20 sulfuric acid, pass the solution through the filter, and collect the filtrate in a 100 ml. volumetric flask. Wash with 1:20 sulfuric acid, add 5 ml. of 3 per cent hydrogen peroxide to the combined filtrate and washings, and dilute to 100 ml. with 1:20 sulfuric acid. Compare with a suitable standard in any convenient way.

**Note.**—If sufficient iron is present to give an appreciable yellow color, add a regulated amount of phosphoric acid (see p. 423) to discharge the color.

### B. STEEL

The following procedure<sup>15</sup> may be used for steels free from vanadium and molybdenum. The effect of iron is compensated by placing an aliquot of the sample solution in the comparison cell. The accuracy of the procedure may be judged by the following figures; samples containing 0.08, 0.25, 0.37 and 0.51 per cent of Ti yielded the respective values 0.082, 0.25, 0.365 and 0.50.

If the transmittancy of the peroxidized solution is determined at two suitable wave lengths (420–440 and 550–580  $m\mu$ ) both titanium and vanadium can be determined in the presence of each other.<sup>15</sup>

#### ¶ Procedure

Dissolve 1–1.25 g. of steel in 50 ml. of 1:1 nitric acid. Boil to expel oxides of nitrogen, add 5 ml. of ammonium persulfate solution (500 g. per liter), and boil to decompose the excess of persulfate. Cool and dilute to 100 ml. in a volumetric flask. Transfer 20 ml. of the mixed solution to a 25 ml. volumetric flask, add 3 ml. of 3 per cent hydrogen peroxide, and dilute to volume with water. Determine the transmittancy of the solution, using as comparison solution 20 ml. of sample solution diluted to 25 ml. with water. For the greatest sensitivity use light of wave length 400–450  $m\mu$ .

The calibration curve should preferably be constructed by taking a titanium-free steel, adding known amounts of titanium, and proceeding as above.

### C. BIOLOGICAL MATERIAL (ANIMAL TISSUES)

#### ¶ Procedure<sup>16</sup>

Ash 50–100 g. of sample and dissolve the residue in concentrated sulfuric acid. Dilute the solution to give an acidity of about 2 *N*, and add sufficient tartaric acid to make its concentration 1–2 per cent and a few milligrams of ferric iron to act as a collector. Add an excess of cupferron (5 per

<sup>15</sup> H. Pinsl, *Angew. Chem.*, **50**, 115 (1937).

<sup>16</sup> L. Maillard and J. Ettori, *Compt. rend.*, **202**, 594 (1936).

cent solution), filter off the precipitate on paper, and wash with 0.2 per cent cupferron solution which is 2 *N* in sulfuric acid. Ignite the precipitate, fuse with a little potassium pyrosulfate and dissolve in dilute sulfuric acid. Add tartaric acid to make its concentration about 1 per cent, nearly neutralize with ammonia, and saturate with hydrogen sulfide. Make the solution ammoniacal, filter off the precipitate of ferrous sulfide, and wash with dilute ammonium sulfide solution. Make the filtrate about 2 *N* in sulfuric acid and boil to remove hydrogen sulfide.

Add a few milligrams of a zirconium salt to the solution and precipitate with cupferron. Filter off the precipitate, wash, ignite, and fuse the residue with 0.1 g. potassium pyrosulfate. Dissolve the melt in 5–10 ml. of 1:20 sulfuric acid, add 1 ml. of 3 per cent hydrogen peroxide, and compare against a standard containing the same amount of potassium sulfate as the sample solution.



## CHAPTER XLV

### TUNGSTEN

The reactions at present available for the colorimetric determination of tungsten are not all that might be desired as far as the requirements of trace analysis are concerned. The thiocyanate method is probably the most generally satisfactory of the methods described below; it is fairly sensitive and specific, but requires the absence of molybdenum and much iron.

#### I. Separations

Fusion of the sample (oxides, silicates, etc.) with sodium carbonate or sodium hydroxide followed by leaching of the melt with water serves to separate tungsten together with molybdenum, chromium, vanadium, arsenic, etc. from iron and other metals forming insoluble hydroxides. Sodium hydroxide precipitation fulfills the same purpose.<sup>1</sup> Molybdenum may be separated from tungsten by precipitation of the former with hydrogen sulfide in dilute acid solution in the presence of tartrate to prevent coprecipitation of tungsten. A little copper may be added as collector for the molybdenum to insure its complete precipitation.

Small amounts of tungsten may be concentrated by adding a little ferric iron or aluminum<sup>2</sup> to the solution and precipitating with ammonia. Extraction of the thiocyanate complex of tungsten in a lower valence with ether should be a useful method for the isolation of tungsten in certain cases; the extracts may be treated as described on p. 383 to bring tungsten into aqueous solution.

#### II. Methods of Determination

##### A. THIOCYANATE-STANNOUS CHLORIDE METHOD

The addition of thiocyanate and stannous chloride to an acid tungstate solution produces a weak greenish color. On the other hand if thiocyanate

<sup>1</sup> A. G. Scobie, *Ind. Eng. Chem., Anal. Ed.*, **15**, 79 (1943), in separating tungsten from much ferric iron, adds the nearly neutral solution of the sample in a thin stream to boiling 20 per cent sodium hydroxide solution and keeps the mixture at the boiling point for thirty minutes before diluting with water and filtering. The precipitate is dissolved in hydrochloric acid and reprecipitated in the same manner. As little as 0.2 mg. of tungsten can be separated in this way from as much as 10 g. of ferric chloride.

<sup>2</sup> In isolating tungsten from very dilute solution (that resulting from the sodium hydroxide precipitation described in the preceding footnote) Scobie (*loc. cit.*) adds enough aluminum ion to the acidified solution to make its concentration about 0.01 per cent and precipitates aluminum hydroxide at the boiling point by adding sodium bicarbonate solution until methyl orange shows its basic color.

and stannous chloride in hydrochloric acid are added to a tungstate solution containing sodium hydroxide a yellow color slowly forms in the acid solution on standing.<sup>3</sup> The original concentration of sodium hydroxide in the solution is not critical; it may vary from 0.05 to 0.5 *N*. Under the conditions described in the procedure below the color intensity is still increasing after two hours, but the increase after one hour is so small that the color can be read at that time. The color development is more rapid if the solution is heated.<sup>4</sup> Beer's law is followed. When very low concentrations of tungsten are involved, it may be advantageous to extract the thiocyanate complex with ethyl ether (*cf.* molybdenum, p. 333).<sup>5</sup>

Molybdenum must be absent. Phosphate in small amounts (as much as 0.25 per cent  $\text{H}_3\text{PO}_4$ ) may be present. Small quantities of iron (up to about 0.3 per cent) are not harmful. Tartrate does not have any ill effect.

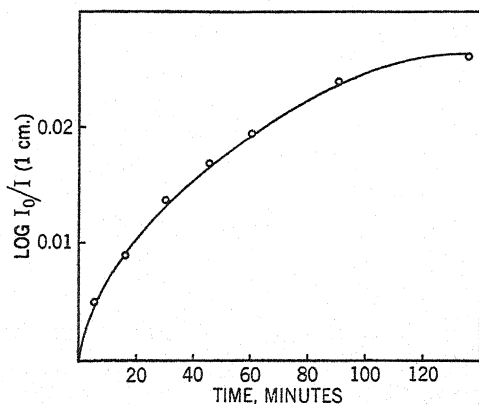


Fig. 65.—Dependence of the color of tungsten-thiocyanate-stannous chloride solution (4 p.p.m. W) on time.

Thus 25 ml. of a solution containing 1 g. of sodium potassium tartrate and 100  $\gamma$  of tungsten showed 95  $\gamma$  of the element when analyzed according to the procedure below. However, if the solution also contains iron the results are high because then the tungsten color develops more rapidly than in a tartrate-free solution.

According to Grimaldi and North,<sup>6</sup> arsenic interferes by slowly giving a brown opalescence or a black precipitate; it can be volatilized as the chloride. Titanium in quantities below 10 mg. in 25 ml. does not interfere; above 10 mg., a yellow color is produced, which is stronger in the presence

<sup>3</sup> F. Feigl and P. Krumholz, *Angew. Chem.*, **45**, 674 (1932).

<sup>4</sup> N. S. Poluektov, *Zavodskaya Lab.*, **10**, 92 (1941); *Chem. Abstracts.*, **35**, 5059 (1941)

<sup>5</sup> Emil Fattu, unpublished work, University of Minnesota.

<sup>6</sup> F. S. Grimaldi and V. North, *Ind. Eng. Chem., Anal. Ed.*, **15**, 652 (1943).

of phosphorus. Nickel, cobalt, chromium, and vanadium interfere because of their color if present in more than small amounts. The color given by  $\text{MoO}_3$  is about  $\frac{1}{25}$  as strong as that given by an equal weight of  $\text{WO}_3$ .

### Special Solutions

*Potassium thiocyanate*, 5 per cent.

*Stannous chloride*, 10 per cent  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in concentrated hydrochloric acid.

*Standard tungsten solution*, 0.0100 per cent W. Dissolve 0.0897 g. of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in water and dilute to 500 ml. The solution may also be prepared by dissolving pure  $\text{WO}_3$  in a slight excess of dilute sodium hydroxide.

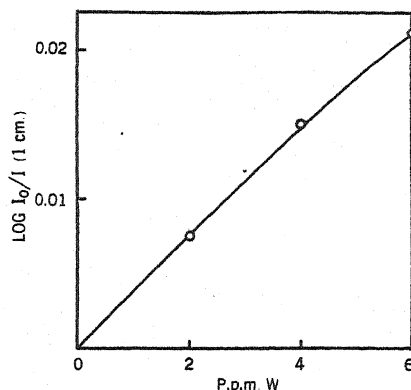


Fig. 66.—Determination of tungsten by the stannous chloride-thiocyanate method (blue filter).

### ¶ General Procedure

Transfer 5 ml. of approximately neutral sample solution, containing up to 0.15 mg. of tungsten, to a 25 ml. volumetric flask and add in succession, mixing after each addition, 1 ml. of 1 *N* sodium hydroxide, 5 ml. of potassium thiocyanate and 10 ml. of stannous chloride solution. Dilute to volume and mix. After one hour obtain the transmittancy of the solution with the aid of a blue filter (maximum transmission at 420  $m\mu$ ). Read the standards after the same time of standing.

When very small quantities of tungsten are present, extract with small portions of ether previously shaken with thiocyanate and stannous chloride and compare the combined extracts in a narrow tube against similar standards (*cf.* p. 335).

### ¶ Procedure for Tungsten in Biological Materials<sup>7</sup>

Transfer 2 ml. of blood, 10 ml. of urine or 2 g. of organ to a Kjeldahl flask and add 4 ml. of concentrated sulfuric acid, 5 ml. of nitric acid, and

<sup>7</sup> J. C. Aull and F. W. Kinard, *J. Biol. Chem.*, **135**, 119 (1940).

5 ml. of 70 per cent perchloric acid. Heat gradually and if charring occurs add more nitric-perchloric acid (equal volumes of each) until the solution clears. Heat until white fumes are no longer evolved, cool the mixture, and dilute with water. Make distinctly alkaline with 40 per cent sodium hydroxide. Boil vigorously for several minutes, cool and dilute to a suitable volume. Filter the solution and take a 5 ml. aliquot ( $<0.15$  mg. W) for analysis according to the general procedure above, omitting however the addition of more sodium hydroxide.

Alternatively (the procedure used by Aull and Kinard) carry out the determination with titanous chloride as reducing agent in place of stannous chloride as follows. To a 5 ml. aliquot (up to 0.1 mg. W) add 1 ml. of 15 per cent potassium thiocyanate, 4 ml. of concentrated hydrochloric acid, and 1 ml. of titanous chloride (boil 1 ml. of 10 per cent titanous chloride with 2 ml. of hydrochloric acid to expel traces of hydrogen sulfide and dilute to 80 ml. with hydrochloric acid). Determine the transmittancy of the solution after 10 minutes, using a filter showing maximum transmission at 420  $m\mu$ .

#### B. THE HYDROQUINONE METHOD<sup>8</sup>

In strong sulfuric acid medium hydroquinone<sup>9</sup> produces a red color with tungsten (VI). Small amounts of water reduce the color intensity markedly. The higher the concentration of hydroquinone in the solution the larger the amount of water that may be present without affecting the color. Thus with 2 g. of hydroquinone, the color intensity begins to decrease when 2 ml. of water are present in 100 ml. of the sulfuric acid (*sp. gr.* 1.84) mixture; with 4 g. hydroquinone no decrease in color is noticed until 6 ml. of water are present in 100 ml.; and with 10 g. of hydroquinone in 100 ml., as much as 10 ml. of water in the mixture has no effect. Beer's law is obeyed. Chloride modifies the color produced (Fig. 67). Nitrate must be absent. Although the reaction product shows maximum absorption at 465  $m\mu$ , it is generally advisable to use light of wave length 570–580  $m\mu$  to avoid error due to traces of organic substances, nitrate, etc. which produce a yellow color.

Titanium gives a color very similar to that produced by tungsten, and no way of preventing its interference is known. Ferric iron, but not ferrous, prevents the reaction of tungsten. Molybdenum (VI) may give a red, brown or blue color depending upon conditions. The interference of molybdenum and ferric iron may be prevented by reduction with stannous

<sup>8</sup> G. Heyne, *Z. angew. Chem.*, **44**, 237 (1931); G. Bogatzki, *Z. anal. Chem.*, **114**, 170 (1938).

<sup>9</sup> A number of phenolic substances (including phenol) react with tungstate in sulfuric acid. Cf. M. E. Defacqz, *Compt. rend.*, **123**, 308 (1896).

chloride. To hinder the reduction of tungsten, phosphoric acid may be added according to Bogatzki. A low concentration of phosphoric acid has no effect, but larger amounts bleach the tungsten color. Aluminum, manganese, tantalum, and copper do not interfere. Vanadium (III), nickel, and chromium (III) do not give a color with the reagent but their own color may be slightly disturbing, unless compensated by the use of an aliquot of the solution in the reference cell.

As an example of the application of the hydroquinone method the procedure for the determination of tungsten in steel will be given (Bogatzki<sup>8</sup>).

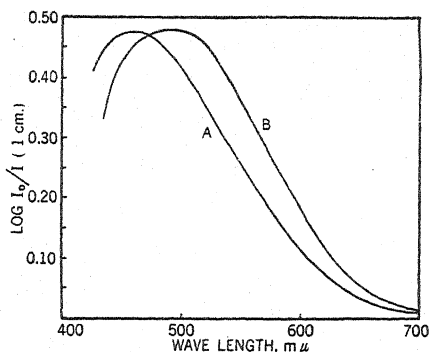


Fig. 67.—Absorption curves of (A) 1 mg. tungsten and 2.5 g. hydroquinone in 100 ml. sulfuric acid, and (B) 1 mg. tungsten, 2.5 g. hydroquinone and 0.32 g. HCl in 100 ml. sulfuric acid. (According to Bogatzki, *loc. cit.*).

### Special Solutions

*Sulfuric-phosphoric acid mixture.* Dilute 200 ml. phosphoric acid (sp. gr. 1.7) and 60 ml. sulfuric acid (sp. gr. 1.84) to 500 ml. with water.

*Stannous chloride.* Dissolve 200 g.  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in water containing 100 ml. hydrochloric acid (sp. gr. 1.19) and dilute to 500 ml. with water.

*Hydroquinone.* Dissolve 10 g. hydroquinone in 80 ml. sulfuric acid (sp. gr. 1.84) and dilute to 100 ml. with sulfuric acid. If any insoluble material remains filter the solution through a sintered glass crucible. Do not use the solution after 2 days.

### Procedure

Dissolve 0.5 g. of steel in 25 ml. of sulfuric-phosphoric acid mixture. Add nitric acid dropwise to oxidize iron, and evaporate to the first fumes of sulfuric acid. Allow the solution to cool somewhat, add 50 ml. of water, and cool to room temperature. Add 5 ml. of stannous chloride and dilute to 100 ml. in a volumetric flask. Transfer 2.00 ml. of the mixed solution to a dry 50 ml. Erlenmeyer flask and add 20 ml. of hydroquinone solution. Cool and after 3 minutes obtain the optical density of the solution, using a 2 cm. cell (for less than 0.5 per cent W) and a filter showing maximum trans-

mission in the vicinity of 570 m $\mu$ . If chromium is present deduct 0.01 per cent W for each 1 per cent of Cr.

To guard against error from the presence of titanium test for this element by adding 10 ml. of hydroquinone solution to 10 ml. of sample solution. Titanium gives a red-orange color and tungsten no color under these conditions.

### C. OTHER METHODS

A number of methods for the determination of tungsten are based on its reduction to colored lower oxides by strong reducing agents. Titanous chloride,<sup>10</sup> and stannous chloride reduce tungstates in acid solutions to insoluble blue oxides remaining in colloidal suspension. Lead in phosphoric acid solutions gives a red color.<sup>11</sup> These reactions are not very sensitive.

Phosphoric acid and vanadate give a yellow color with tungstate (phosphotungstovanadic acid, p. 440). Again the sensitivity is rather low, and even small amounts of iron hinder the development of the color.

Rhodamine B reacts with tungsten (VI) in dilute hydrochloric acid.<sup>12</sup> The color change is from yellow-red to violet. A rough quantitative method ( $\pm$  20 to 30 per cent) has been worked out by Heyne.<sup>12</sup> Relatively much molybdenum may be present.

<sup>10</sup> A. Travers, *Compt. rend.*, **165**, 408 (1917); **166**, 416 (1918).

<sup>11</sup> A. Petrovskii, *J. Chem. Ind. Moscow*, **7**, 905 (1930).

<sup>12</sup> E. Eegriwe, *Z. anal. Chem.*, **70**, 400 (1927); G. Heyne, *Z. angew. Chem.*, **44**, 237 (1931).

## CHAPTER XLVI

### URANIUM

The colorimetric methods for uranium are relatively insensitive and not well suited for the determination of very small amounts of the element. However, a fluorimetric method is available which can be used for the determination of extremely minute amounts.

#### I. Separations

Uranium may be separated from the metals of the hydrogen sulfide group by the precipitation of these in an acid solution containing tartrate. Ammonium sulfide does not precipitate uranium from a solution containing ammonia and tartrate, and a separation may thus be effected from iron and other metals yielding sulfides under these conditions.

Uranium (VI) forms a soluble complex with alkali metal carbonates. Ferric iron, aluminum, and other metals may be precipitated with ammonium carbonate, and uranium left in solution. Traces of iron remain in solution and may give rise to difficulties when very small amounts of uranium are to be determined, because iron reacts with some of the colorimetric reagents for uranium. A fusion with sodium carbonate followed by leaching with water will presumably separate uranium from iron and other metals yielding slightly soluble precipitates under the conditions.

Electrolysis with a mercury cathode in sulfuric acid solution serves to separate iron, and has the advantage over other methods of not being subject to loss of uranium by coprecipitation. Cupferron precipitates iron, vanadium, titanium, etc. but not hexavalent uranium in dilute sulfuric acid solution; quadrivalent uranium is precipitated.

Very small amounts of uranium can be isolated by coprecipitation with ferric or aluminum hydroxide,<sup>1</sup> or with the phosphates of iron and aluminum.<sup>2</sup> See p. 434.

#### II. Methods of Determination

##### A. THE FLUORESCENCE METHOD

Uranium (VI) shows rather weak fluorescence in aqueous solution. A solid solution of uranium in sodium fluoride shows strong yellowish fluores-

<sup>1</sup> W. D. Urry, *Am. J. Sci.*, **239**, 191 (1941).

<sup>2</sup> Uranium can be separated from vanadium (V) by precipitation as phosphate from a nearly neutral (very slightly acid) solution. Aluminum phosphate may be used as collector. See J. A. Tschernichow and E. Guldina, *Z. anal. Chem.*, **96**, 257 (1934).

cence<sup>3</sup> in ultraviolet light. Minute amounts of uranium may be determined by evaporating the sample solution with a known weight of sodium fluoride, mixing the dry residue by grinding in an agate mortar, fusing a portion of the powder in a platinum loop, and comparing the bead so obtained against standard beads in ultraviolet light. The comparison may be made more accurately by photographing the fluorescence spectra of the sample and standard beads, and measuring the darkening with a microphotometer.<sup>4</sup> A micro pastil press may be used to obtain beads constant in weight to 5 per cent. The intensity of the fluorescence is proportional to the amount of uranium present in the range  $10^{-6}$  to  $5 \times 10^{-3}$  mg. of U (25 mg. bead). As little as  $10^{-7}$  mg. of uranium can be detected.

The solution in which uranium is to be determined by this method should in general be free from foreign elements, because some of these may seriously reduce the intensity of the fluorescence. Silica, titanium, thorium, iron, and sulfate all interfere; the effect of manganese is less serious. Potassium, magnesium, and barium in small amounts are without effect, but calcium interferes seriously. As little as 6 per cent of calcium fluoride in the bead nearly completely extinguishes the fluorescence, 2 per cent reduces it 83 per cent, and 1 per cent reduces it 45 per cent. In the presence of calcium the hue of the fluorescence is green; as little as 1 per cent of calcium suffices to produce a change in hue visible to the eye and gross errors can thus be avoided.<sup>5</sup>

In the following paragraphs the application of the fluorescence method to the determination of uranium in various natural samples will be briefly described.

### 1. Sea Water<sup>4,6</sup>

The sample (1–20 liters) is weakly acidified and concentrated by evaporation, the calcium sulfate separating being filtered off. The concentrated solution of salts is boiled to remove carbon dioxide, ferric chloride is added as collector and ferric hydroxide precipitated with carbonate-free ammonia. About 90 per cent of the uranium is carried down with the iron precipitate. The filtrate is acidified with hydrochloric acid, ferric chloride added and ferric hydroxide precipitated as before. In most cases a third precipitation is unnecessary. The combined iron precipitates are dissolved

<sup>3</sup> L. Papish and L. E. Hoag, *Proc. Natl. Acad. Sci. U. S.*, **13**, 726 (1927); E. L. Nichols and M. Slattery, *J. Optical Soc. Am.*, **12**, 449 (1926).

<sup>4</sup> F. Hernegger and B. Karlik, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. IIa*, **144**, 217 (1934).

<sup>5</sup> I. Lahner, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. IIa*, **148**, 149 (1939).

<sup>6</sup> One to two micrograms of U per liter of sea water was found.



in hydrochloric acid and the iron precipitated with ammonia to eliminate salts of the alkali metals. Iron is then separated from uranium by triple precipitation with ammonium carbonate. The filtrates are evaporated to dryness, and ammonium salts expelled by ignition in platinum. The residue, consisting mostly of silica, is treated with hydrofluoric and sulfuric acids and the latter volatilized. The residue is dissolved in a little hydrochloric acid and the solution evaporated to dryness. A weighed amount (*e.g.*, 1 g.) of sodium fluoride together with water and a drop or two of hydrofluoric acid are added and the mixture evaporated to dryness. The powder is mixed by grinding in an agate mortar and a bead of about 25 mg. obtained by heating the sodium fluoride in a platinum wire loop. Excessive heating should be avoided in the formation of the bead. It suffices to heat just to the point where the globule appears clear.

The procedure was tested by adding a known amount of uranium to a sample in which uranium had been determined. The added amount was recovered within the limits of error.

### 2. Carbonate Rocks<sup>5,7</sup>

The sample (2–5 g.) is dissolved in dilute hydrochloric acid. Any residue remaining is treated with hydrofluoric and sulfuric acids, the latter evaporated, the residue dissolved in hydrochloric acid, and this added to the main solution. Uranium is then coprecipitated with ferric hydroxide and the iron separated with ammonium carbonate as in the case of sea water.

### 3. Silicates, Silicate Rocks, and Glass.<sup>8</sup>

The sample (1 g.) is fused with sodium carbonate and silica separated by treating the melt with hydrochloric acid and evaporating to dryness on the water bath. The silica residue is volatilized with hydrofluoric acid and any remaining material is decomposed by fusion with a 10:3 mixture of sodium carbonate and borax; the solution of this melt is combined with the filtrate from the silica. The metals of the hydrogen sulfide group are separated in the usual manner; a pressure bottle is used in the hydrogen sulfide precipitation if molybdenum is present. Metals such as chromium and nickel which interfere in the fluorescence determination are separated by repeated precipitation with ammonium sulfide. Uranium is then precipitated with other metals by the addition of pure carbonate-free ammonium hydroxide; in the second precipitation a little ferric chloride is added to insure complete precipitation of uranium. Next uranium is separated from the other

<sup>7</sup> Amounts of uranium varying from  $10^{-6}$  to  $10^{-4}$  per cent were found in limestones and dolomites of the Austrian Alps.

<sup>8</sup> J. Hoffmann, *Sprechsaal*, 73, 153 (1940); *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. IIa*, 148, 189 (1939).

hydroxides by treating the hydrochloric acid solution with ammoniacal ammonium carbonate. This precipitation is repeated, and the solution heated a long time in the second precipitation to make certain the precipitation of any calcium carbonate. The uranium-containing solution is evaporated in a platinum dish in the presence of hydrofluoric acid. One-half to one gram of sodium fluoride is added together with water, the solution evaporated, and the residue ignited. The latter is transferred to an agate mortar and ground well to assure homogeneous distribution of uranium in the sodium fluoride. A bead of sodium fluoride is then obtained on a platinum wire and comparison made against standard beads. The uranium content of igneous rocks may be expected to fall in the range  $10^{-3}$  to  $10^{-6}$  per cent. A series of beads containing from  $5 \times 10^{-3}$  to  $10^{-6}$  mg. U per 25 mg. bead may be used in the comparison.

#### 4. Organic Materials

The following is a resume of the method used by Hoffman<sup>9</sup> in determining uranium in animal tissues. The sample is ashed, the ash dissolved in nitric acid, and phosphate removed by precipitation with tin. The excess tin is precipitated with hydrogen sulfide and the filtrate treated with hydroxylamine hydrochloride and an excess of ammonia. The filtrate is evaporated and the residue treated with fuming nitric acid. Uranium is then precipitated with pure ammonia after the addition of a little ferric chloride. The precipitate is dissolved in acid and iron precipitated with an ammoniacal solution of ammonium carbonate. The precipitation is repeated, the filtrate evaporated to dryness and the residue ignited. Sodium fluoride solution is then added, evaporated, and a bead of fused sodium fluoride obtained as described above.<sup>10</sup>

#### B. THE HYDROGEN PEROXIDE METHOD

Hydrogen peroxide gives a yellow color with uranium (VI) in sodium or ammonium carbonate solution. The reaction is not very sensitive but may be of value on occasion, since it may be applied to the filtrate of a sodium carbonate precipitation or fusion. It has been suggested as the basis of a method for the determination of uranium in silicate rocks;<sup>11</sup> the lower limit of such a method would lie in the neighborhood of 0.01 per cent U. The effect of chromium (VI) can be compensated by using an

<sup>9</sup> J. Hoffmann, *Wien. tierärztl. Monatsschr.*, **28**, 561 (1941).

<sup>10</sup> The minute amounts of uranium that can be determined in this way are indicated by the uranium contents found in cattle (Hoffmann): blood,  $1.6 \times 10^{-13}$  g. /ml.; muscle,  $4 \times 10^{-11}$  g. /g.; bones  $1.3 \times 10^{-8}$  g. /g.

<sup>11</sup> O. Hackl, *Z. anal. Chem.*, **119**, 321 (1940). Cf. E. A. Arnold and A. R. Pray, *Ind. Eng. Chem., Anal. Ed.*, **15**, 294 (1943).

aliquot of the sample in the comparison cell of a photoelectric photometer. Molybdenum (VI) and vanadium (V) also give yellowish colors with hydrogen peroxide but these are much less intense than that given by uranium. Cerium (III, IV) gives a strong yellow color with hydrogen peroxide in carbonate solution (p. 188). Fluoride and phosphate have no effect in small amounts, but larger quantities (in the neighborhood of 0.1 g. of the ammonium salt in 50 ml.) diminish the color intensity. Silicate has practically no effect.

### ¶ Procedure

Add 5 ml. of 10 per cent sodium carbonate solution and 2 ml. of 3 per cent hydrogen peroxide (prepared by dilution of 30 per cent solution) to an approximately neutral uranium solution containing a suitable amount of

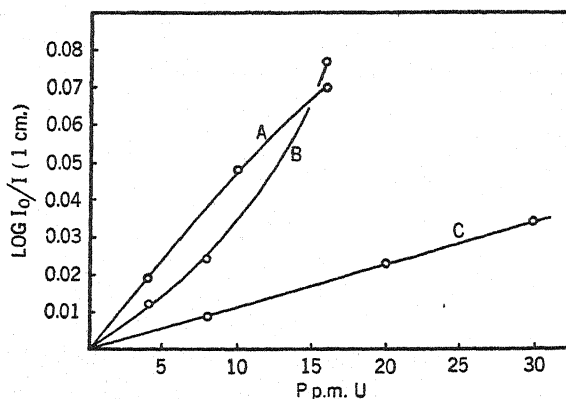


Fig. 68.—Determination of uranium. A. Diethyldithiocarbamate method. B. Ferrocyanide method (neutral solution). C. Hydrogen peroxide method. Blue filter (Wratten 47) used in each case.

uranium (cf. Fig. 68) and dilute to 25 ml. with water. Use a blue filter (450  $m\mu$ ) in determining the transmittancy of the solution. The standard uranium solution can be prepared from uranyl nitrate ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{U} = 2.11$ ).

### C. THE FERROCYANIDE METHOD

Ferrocyanide ion yields slightly soluble brown uranyl ferrocyanide in neutral or slightly acid medium which may be used for the colorimetric determination of uranium. In the writer's limited experience with the method, reproducible results are not easily obtained with low concentrations of uranium in dilute mineral acid medium.<sup>12</sup> The color develops

<sup>12</sup> Five ml. of 10 per cent potassium ferrocyanide were added to about 15 ml. of uranium solution containing 1 ml. of 1 *N* sulfuric acid and the solution diluted to 25 ml. A protective colloid was not added.

slowly, and frequently turbid solutions result. In neutral solution the color is more reproducible although less strong and the liquid does not readily become turbid. Beer's law is not followed (Fig. 68, curve B obtained with a green filter). The addition of ammonium acetate to yield an approximately neutral solution is not permissible because the color then is greatly weakened. A final potassium ferrocyanide concentration of 2 per cent is satisfactory. The solution may be read 10 or 15 minutes after the addition of ferrocyanide. Traces of iron and copper interfere seriously in this method.

#### ¶ Procedure

To 10–15 ml. of sample solution (0.1 to 0.5 mg. U) as nearly neutral as possible (not more than 0.02 *N* in mineral acid) add 5 ml. of potassium ferrocyanide (10 per cent solution containing 1 per cent of sodium sulfite) dilute to 25 ml., and determine the extinction after 15 minutes, using a blue filter. The standards must have the same acidity and salt concentration as the sample solution.

#### D. THE DIETHYLDITHIOCARBAMATE METHOD

The addition of sodium diethyldithiocarbamate to a neutral uranyl solution produces a stable yellow color which is suitable for the determination of uranium if iron and copper are absent. It is very important that the sample solution be neutral before addition of the reagent. A slightly acid reaction (*pH* 6) causes the yellow color to fade quite rapidly. The initial color intensity is greater in slightly acid than in neutral solution. The addition of a little sodium carbonate discharges the color.

#### ¶ Procedure

Add 5 ml. of 20 per cent ammonium acetate solution and then 1 ml. of 1 per cent sodium diethyldithiocarbamate to the sample solution which should contain less than the equivalent of 0.1 ml. of 6 *N* sulfuric or hydrochloric acid. Dilute to 25 ml. with water and determine the extinction after 5 minutes (use a blue filter).

#### E. OTHER METHODS

Sodium salicylate produces a red-brown color in neutral uranyl solutions.<sup>13</sup> The reaction is not particularly sensitive and minute amounts of iron interfere. Various phenolic acids such as tannic and gallic yield brown colorations with uranium in solutions containing sodium acetate (the latter should be added after the acid).<sup>14</sup> Again the color intensity is not strong and iron interferes badly.

<sup>13</sup> Müller, *Chem. Ztg.*, **43**, 739 (1919).

<sup>14</sup> P. N. Das-Gupta, *J. Indian Chem. Soc.*, **6**, 763 (1929).

## CHAPTER XLVII

### VANADIUM

#### I. Separations

A useful method for the separation of vanadium from iron, titanium, etc. involves fusion of the sample with sodium carbonate (together with a little potassium nitrate if necessary) and leaching of the melt with water. Molybdate, tungstate, phosphate, arsenate, chromate, and a trace of iron accompany vanadate into the filtrate.

Cupferron in dilute (1:10) sulfuric acid medium precipitates quinquevalent vanadium as well as iron, titanium, zirconium, and some other metals. Aluminum, chromium, uranium (VI), arsenic, and phosphorus are not precipitated. If chromium is present in the sexivalent condition it should be reduced by the addition of hydrogen peroxide followed by boiling to destroy the excess of the latter. For the isolation of vanadium from highly dilute solutions, iron may be added to serve as a collector if it is not already present.<sup>1</sup> From the standpoint of trace analysis it is worth noting that vanadium cupferrate, like most other cupferrates, can be extracted with ether and chloroform.

In a slightly basic solution, vanadate, chromate, molybdate, tungstate, arsenate, and phosphate can be precipitated with mercurous nitrate.<sup>2</sup> This separation has been used in the determination of small amounts of vanadium in silicate rocks.

Vanadium in the quinquevalent state is coprecipitated with ammonium phosphomolybdate.<sup>3</sup>

Electrolysis with a mercury cathode in dilute sulfuric acid solution serves to separate vanadium from iron, chromium, molybdenum, copper, nickel, etc. Uranium and phosphorus remain in the aqueous solution with vanadium.

Small amounts of vanadium (IV and V) are coprecipitated with ferric iron and aluminum in an ammonium hydroxide precipitation. Iron is a better collector than aluminum. Because of the similarity in the ionic

<sup>1</sup> L. W. Strock and S. Drexler, *J. Optical Soc. Am.*, **31**, 167 (1941), found that the precipitation of vanadium (1:2 000 000) by cupferron was complete in the presence of iron at acidities ranging from pH 7 to 15 per cent HCl. A high neutral salt concentration (20 per cent K, Na, Ca, Mg chlorides) did not interfere.

<sup>2</sup> W. F. Hillebrand, *J. Am. Chem. Soc.*, **20**, 454 (1898).

<sup>3</sup> J. R. Cain and J. C. Hostetter, *J. Ind. Eng. Chem.*, **4**, 250 (1912); *J. Am. Chem. Soc.*, **43**, 2552 (1921).

radii of phosphorus (V) and vanadium (V), it may be expected that ferric phosphate will be a good collector for vanadate.

A good method for the isolation of minute amounts of quinquevalent vanadium in certain cases is based on the extraction of its 8-hydroxyquinoline compound,<sup>4</sup>  $V_2O_5(C_9H_6ON)_4$ , with chloroform from a weakly acid solution (pH 4-5); chromium (VI) is not extracted.<sup>5</sup> After evaporation of the chloroform the residue can be fused with sodium carbonate and the vanadium transformed into vanadate. Ferric iron and molybdenum (VI) are also extracted. This method of separation is therefore not applicable to ferrous materials. Aluminum, silicate, phosphate, fluoride, etc. do not hinder the extraction of vanadium. Tungsten gives a precipitate with oxine (insoluble in chloroform), except when present in very small amounts, and should therefore be absent. For the behavior of other metals with oxine see p. 95. Some results showing the satisfactory separation of vanadium in the presence of 100-200 times as much chromium in the analysis of silicates are given on p. 445.

## II. Methods of Determination

### A. THE PHOSPHOTUNGSTATE METHOD<sup>6</sup>

A sensitive and selective method for the determination of vanadium is based on the formation of yellow soluble phosphotungstovanadic acid by the addition of phosphoric acid and sodium tungstate to an acid vanadate solution. The strongest color is obtained when the molecular ratio of phosphoric acid to sodium tungstate lies in the range 3:1 to 20:1, and the tungstate concentration in the sample solution is 0.01 to 0.1 *M*. A final concentration of phosphoric acid equal to 0.5 *M* and of sodium tungstate equal to 0.025 *M* is recommended (Wright and Mellon<sup>6,7</sup>).

The acidity of the solution may vary over a fairly wide range. A solution 2.4 *N* in sulfuric, nitric or hydrochloric acid, and containing 50  $\gamma$  of vanadium per ml. gives virtually the same color intensity as a solution containing no acid, provided it is boiled. In the cold, a brownish color is obtained which after several hours goes over into the normal yellow color of phosphotungstovanadic acid. The higher the acid concentration the stronger is the brownish color. Boiling hastens the attainment of equi-

<sup>4</sup> R. Montequi and M. Gallego, *Anales soc. españ. fís. quim.*, **32**, 134 (1934).

<sup>5</sup> E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 336 (1936).

<sup>6</sup> A. P. Vinogradov, *Compt. rend. acad. sci. U. R. S. S.*, **1931A**, 249. E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 336 (1936). E. R. Wright and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 251 (1937). Cf. H. H. Willard and P. Young, *Ind. Eng. Chem.*, **20**, 764 (1928).

<sup>7</sup> The statements in the discussion following above are based on the findings of these authors in a comprehensive study of the phosphotungstate method.

librium. More dilute vanadium solutions—less than 10  $\gamma$  of V per ml.—need not be boiled if the acidity is in the neighborhood of 0.5 *N* and iron is absent; the maximum color is not developed immediately in the cold, but the difference is not great enough to be of importance in visual comparison.

The following substances, in the amount indicated per 100 ml. of sample solution, have no appreciable effect on the vanadium color: NaCl (3 g.); NaNO<sub>3</sub> (5 g.); Mg, Ca, Sr, Ba, Zn, Cd, Hg<sup>II</sup>, Al, Pb, As<sup>V</sup>, acetate, Br<sup>-</sup> (all 0.5 g.); Ag (0.1 g.); Th (0.01 g.); SiO<sub>2</sub> (0.05 g. as Na<sub>2</sub>SiO<sub>3</sub>); tartrate, citrate, oxalate (0.1 g. of anion); CN<sup>-</sup> (0.02 g.); H<sub>3</sub>BO<sub>3</sub>, F.

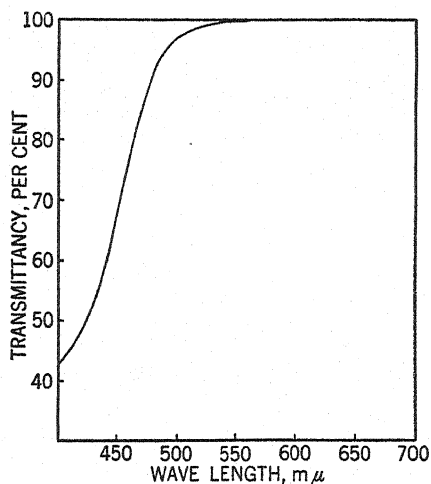


Fig. 69.—Transmission curve of phosphotungstovanadic acid (10 p.p.m. V, 1 cm. cell). (According to Wright and Mellon.)

In addition to ions which are themselves colored, such as chromate, copper, cobalt, etc., the following interfere:

1. Potassium and especially ammonium ions give slightly soluble phosphotungstates.
2. Titanium, zirconium, bismuth, antimony and tin give slightly soluble phosphates or basic salts except in very low concentrations.
3. Molybdenum (VI) gives a yellow color with the reagent, which however only becomes serious at relatively high concentrations (> 500  $\gamma$  per ml. when vanadium concentration is 2.5  $\gamma$  per ml.) Cf. Table 60.
4. Iodide, thiocyanate, etc. reduce phosphotungstic acid.

Ferric ion in small amounts is not harmful if the solution is boiled. Ten milligrams of iron (III) in 100 ml. of cold solution imparts a brownish hue, but this disappears if the solution is boiled. However in a concentration greater than 100 mg. per 100 ml. iron begins to interfere even if more phosphoric acid is added.

Phosphotungstovanadic acid is quite stable in solution. No change in the color intensity takes place in 24 hours, but after 2 weeks a diminution of about ten per cent occurs.

Some figures obtained by the phosphotungstic acid method in the determination of vanadium by colorimetric titration are given in Table 60.

#### Special Solutions

*Sodium tungstate, 0.5 M.* Dissolve 16.5 g. of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in water and dilute to 100 ml.

*Standard vanadium solution.* Dissolve 1.785 g. of pure  $\text{V}_2\text{O}_5$ , previously ignited at  $500^\circ\text{C}$ ., in a slight excess of sodium hydroxide, then add a slight excess of sulfuric acid and dilute to 1 liter. This solution will contain 1.00 mg. of vanadium per ml. If there is any doubt about the purity of the vanadium pentoxide, acidify a 50 ml. portion of the solution with sulfuric acid, reduce with sulfur dioxide in the usual manner, expel the excess of sulfur dioxide by boiling and titrate with 0.05 or 0.1 *N* potassium permanganate.

Dilute the above vanadium solution further, conveniently to give a solution containing 0.01 mg. V per ml.

TABLE 60

DETERMINATION OF VANADIUM BY THE PHOSPHOTUNGSTIC ACID METHOD<sup>a</sup>  
(Colorimetric titration in  $1.8 \times 15$  cm. flat-bottomed tubes; 10–15 ml. of solution)

Addition	Vanadium taken $\gamma$	Vanadium found $\gamma$	Error $\gamma$
	3	3	0
	5	4	-1
	12	12	0
	20	21	+1
	50	51	+1
0.5 mg. Mo (VI)	20	22	+2
1.0 mg. Mo (VI)	20	23	+3
10.0 mg. Mo (VI)	20	26	+6

#### ¶ Procedure

Make the solution approximately 0.5 *N* in sulfuric, nitric or hydrochloric acid, and add 1.0 ml. of 1:2 phosphoric acid and 0.5 ml. of sodium tungstate solution for each 10 ml. of sample solution. Heat to boiling (this is not necessary if only small amounts of vanadium are present and iron is absent—see p. 446), cool, dilute to volume, and determine the extinction of the solution at  $400 m\mu$  (Fig. 69). If small amounts of colored ions such as nickel, cobalt, and dichromate are present use an aliquot of the original sample solution in the reference cell (p. 62). At  $400 m\mu$ , an extinction of

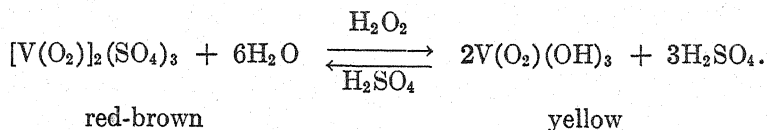
<sup>a</sup> Selected figures from E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 336 (1936).



0.001 corresponds to approximately 0.03  $\gamma$  V per cm.<sup>2</sup> In visual colorimetry the solution should contain more than 1  $\gamma$  V per cm.<sup>2</sup> cross section.

### B. THE PEROXIDE METHOD

The red-brown color obtained when an acid solution of quinquivalent vanadium is treated with hydrogen peroxide is frequently ascribed to the formation of pervanadic acid ( $\text{HVO}_4$ ), but according to Meyer and Pawletta<sup>9</sup> the compound  $\text{H}_3[\text{V}(\text{O}_2)\text{O}_3]$  is formed, and the following equilibrium exists in a sulfuric acid solution:



A large excess of drogen peroxide changes the color of the solution from red-brown to yellow and reduces the color intensity.

Other metals giving colors with hydrogen peroxide are titanium, and molybdenum (VI). The titanium color can be bleached by fluoride, which in moderate amounts does not affect the vanadium color. The interference of iron (III) may be prevented by the addition of phosphoric acid or fluoride. Chromium (VI) gives a blue color which soon fades, leaving an almost colorless solution when small amounts are present. Iodide and bromide must be absent.

Wright and Mellon<sup>10</sup> in their study of the peroxide method for vanadium found that with a hydrogen peroxide concentration of 0.03 per cent, the sulfuric acid concentration could vary between 0.6 and 6 *N* without any appreciable effect on the color; below 0.6 *N* acidity the full color is not developed and above 6 *N* it fades. With higher peroxide concentrations the acidity must be increased to permit development of maximum color intensity. In the range 0.006 to 0.09 per cent hydrogen peroxide concentration the color intensity remains constant (solutions 1.5 *N* in sulfuric acid). Neutral salts such as sodium sulfate or sodium chloride have little effect on the color. The color is fairly stable; under the condition recommended below there should be no appreciable change in color intensity in 2 or 3 days. Beer's law is obeyed.

### ¶ Procedure

The solution should be free from the interfering elements mentioned above. The effect of metals such as nickel, cobalt, etc. and very small amounts of chromium can sometimes be compensated by adding like

<sup>9</sup> J. Meyer and A. Pawletta, *Z. anal. Chem.*, **69**, 15 (1926).

<sup>10</sup> E. R. Wright and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 375 (1937).

amounts to the comparison solution; when a photometer is used, an aliquot of the sample solution can be put in the reference cell. Vanadium must be present in the quinquevalent form.

Make the solution 1 to 2 *N* in sulfuric acid and add 0.25 ml. of 3 per cent hydrogen peroxide for each 10 ml. of sample, and compare against a standard vanadium solution having the same acidity and containing the same amount of peroxide. If titanium is present add hydrofluoric acid (say 1 ml. for 10–20 ml. of solution). This will decolorize ferric iron also. If titanium is absent, phosphoric acid may be used in place of hydrofluoric acid for the decolorization of iron. If hydrofluoric acid is added, the comparison should be made in inexpensive tubes by the standard series method.

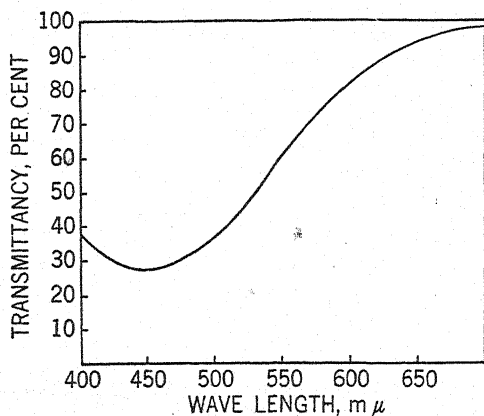


Fig. 70.—Transmission curve of peroxidized vanadium in sulfuric acid solution (20 p.p.m. V, 5 cm. cell). (According to Wright and Mellon.)

### C. OTHER METHODS

8-Hydroxyquinoline reacts with quinquevalent vanadium as already mentioned to give a strongly colored violet-black compound which can be extracted by various organic solvents. It has been proposed to utilize this reaction in the determination of vanadium in water as follows.<sup>11</sup> The sample (50 ml.) is made acid to Congo red with sulfuric acid and 5 drops of a 2.5 per cent solution of 8-hydroxyquinoline in 20 per cent citric acid are added. The solution is shaken with 10 ml. of isoamyl alcohol to extract the quinolate. Copper, but not iron, interferes. Beer's law is followed.

8-Hydroxyquinoline-5-sulfonic acid gives a brown color with metavanadate and has been used for determining concentrations of vanadium of the order 1 p.p.m.<sup>12</sup> Iron reacts similarly.

<sup>11</sup> J. M. Bach and R. A. Trelles, *Bol. obras sanit. nacion Buenos Aires*, **5**, 127 (1941). *Chem. Abstracts*, **36**, 859 (1942); **35**, 545 (1941).

<sup>12</sup> J. Molland, *Compt. rend.*, **210**, 144 (1940).

A mixture of molybdate and phosphoric acid gives a yellow color with vanadate.<sup>13</sup> The reaction is analogous to the phosphotungstate reaction described above. Molybdate alone gives a yellow color with vanadate in neutral solution.<sup>14</sup>

In concentrated sulfuric acid vanadate reacts with strychnine to yield a violet color passing into orange.<sup>15</sup> Iron must be absent, but titanium, molybdenum, and tungsten do not interfere.

Diphenylamine, diphenylamine sulfonic acid, etc. are oxidized by vanadate to blue compounds in acid solution.<sup>16</sup> Many oxidizing agents give the same color. Ferric iron does not react in the presence of phosphoric acid.

Vanadium has been determined as thiovanadate (red) in iron ores, slags, etc. by adding sodium sulfide to an alkaline vanadate solution.<sup>17</sup>

### III. Applications

#### A. SILICATE ROCKS

The phosphotungstate method may be applied with advantage in the determination of the small amounts of vanadium occurring in silicate rocks. Vanadium is isolated from the solution of the sodium carbonate melt by the 8-hydroxyquinoline-chloroform extraction procedure mentioned above. As much as 1 per cent  $\text{Cr}_2\text{O}_3$  and several per cent fluorine do not interfere. Molybdenum is normally not present in sufficiently large amounts to affect the results (*cf.* Table 60). The following results show the reliability of the method (first figure gives the percentage of  $\text{V}_2\text{O}_5$  added to a synthetic basic rock, the second the percentage found): 0.0021, 0.0027; 0.004, 0.005; 0.015, 0.014; 0.042, 0.040; 0.006, 0.005 (1%  $\text{Cr}_2\text{O}_3$ ); 0.0120, 0.0115 (1%  $\text{Cr}_2\text{O}_3$ ).

#### ¶ Procedure

Fuse 1 g. of 100-mesh rock powder with 5 or 6 g. of anhydrous sodium carbonate in platinum in the usual way. After complete decomposition allow the crucible to cool to room temperature, add a few milliliters of water and heat to boiling to loosen the cake. Transfer the latter to a small Pyrex beaker, rinse the crucible, and add a few drops of alcohol and 30–40 ml. of water to the beaker. Heat on the steam bath, and hasten disintegration of the cake by crushing and grinding with a flattened glass rod. When the residue has been entirely disintegrated and manganate reduced,

<sup>13</sup> G. Bogatzki, *Arch. Eisenhüttenw.*, **12**, 539 (1939).

<sup>14</sup> A. G. Woodman and L. L. Cayvan, *J. Am. Chem. Soc.*, **23**, 105 (1901).

<sup>15</sup> A. W. Gregory, *Chem. News*, **100**, 221 (1909).

<sup>16</sup> V. L. Meaurio, *Ann. chim. anal.*, **23**, 47 (1918).

<sup>17</sup> E. Stengel, *Tech. Mitt. Krupp Forschungsber.*, **2**, 93 (1939). *Chem. Abstracts*, **33**, 9189 (1939).

filter the solution through a fine grained paper and wash with hot 1 per cent sodium carbonate solution. Dilute the filtrate and washings to 100 ml. in a volumetric flask.

Pipet 10 or 25–50 ml. (the former volume for basic rocks, the latter for siliceous rocks) of the mixed solution into a small Erlenmeyer flask and add a drop or two of methyl orange indicator solution. Then add 4 *N* sulfuric acid from a buret until the solution assumes the intermediate color of the indicator. Swirl the solution to liberate carbon dioxide and transfer to a small separatory funnel. Add 2–3 drops of 8-hydroxyquinoline solution (2.5 per cent in 1:8 acetic acid) for 10–25 ml. of sample and 2–3 ml. of reagent quality chloroform. Shake for 1 minute to extract the blackish vanadium-oxine compound, allow the chloroform to settle, and draw it off into a platinum crucible. Rinse out the stem of the funnel with a milliliter of chloroform. Then repeat the extraction with 8-hydroxyquinoline and chloroform as before until the last portion of chloroform shows only a faint yellow color due to the reagent itself.

Add 0.1 g. of anhydrous sodium carbonate to the crucible containing the combined extracts, and evaporate off the chloroform at a low temperature. Heat the crucible with a flame to destroy organic matter and finally apply the full heat of the burner for 1 or 2 minutes to fuse the sodium carbonate. Vanadium is thus converted into sodium vanadate. Dissolve the melt in a few milliliters of water. The solution should be clear; if it is not, filter through a small porous porcelain or sintered glass crucible. If the vanadium is to be determined by colorimetric titration or the standard series method, transfer the solution to a flat-bottomed tube having a cross-section of about 2 cm.<sup>2</sup> and a volume of about 25 ml. (p. 42). The volume of the solution may be 5–10 ml. Add 1.0 ml. of 4 *N* sulfuric acid, 1.0 ml. of 1:2 phosphoric acid, and 0.5 ml. of 0.5 *M* sodium tungstate solution. Compare against standards similarly treated.

If a photometer is used, transfer the solution to a 10 or 25 ml. volumetric flask and treat as described in the general procedure, p. 442.

**Notes.**—1. Vanadium can be determined with fair accuracy directly without previous separation with 8-hydroxyquinoline if its amount is not too small and chromium is absent. The results tend to be low as shown by the following figures obtained on various rocks (the first figure is the percentage of  $V_2O_5$  obtained by 8-hydroxyquinoline separation, the second the percentage obtained by direct colorimetric determination in the filtered sodium carbonate extract); 0.042, 0.036; 0.026, 0.023; 0.029, 0.031; 0.062, 0.055; 0.044, 0.039; 0.245, 0.245 (magnetite-ilmenite).

2. There appears to be no appreciable retention of vanadium in the leached residue. Thus in a basic rock containing 0.060 per cent  $V_2O_5$ , re-fusion of the washed residue from the first sodium carbonate fusion yielded an additional 0.001 per cent  $V_2O_5$ .

3. The addition of potassium nitrate in the fusion is usually not necessary.

## B. IRON AND STEEL

In the following method, vanadium is first separated from the bulk of the iron by addition of sodium bicarbonate to the acid solution of the sample<sup>18</sup>; the relatively small precipitate of iron contains the vanadium as well as chromium, titanium, etc. The washed precipitate is fused with sodium peroxide, the melt is extracted with water and the solution boiled to precipitate titanium completely. The filtrate contains vanadate together with chromate. Vanadium can then be determined by the peroxide or phosphotungstate method, a separation from chromate first being made if necessary.

¶ Procedure<sup>19</sup>

Transfer 5 g. of sample to a 250 ml. Erlenmeyer flask, add 60 ml. of 1:9 sulfuric acid and boil until reaction is complete. Dilute the solution with about 50 ml. of hot water and add an 8 per cent sodium bicarbonate solution from a buret until a permanent precipitate is produced, and then 2 ml. in excess. Boil for 1 minute, allow the precipitate to settle, filter through a fast filter, and without delay wash the flask and precipitate twice with hot water. Disregard any cloudiness in the filtrate. Ignite the residue in a nickel crucible, mix it with about 10 times its volume of sodium peroxide, and fuse. Cool and dissolve the melt in 50 ml. of cold water. Add 0.5 g. of sodium peroxide to the solution, heat to boiling and boil for 10 minutes; allow to stand on the steam bath for one-half hour. Filter through asbestos and wash with a cold solution containing 2 per cent sodium hydroxide and 1 per cent sodium sulfate. Dilute the filtrate and washings to 100 ml.

If the chromium content of the solution is low, vanadium may be determined directly in a suitable aliquot by the peroxide or phosphotungstate method according to the directions given on p. 443 or p. 442. If chromium is present in appreciable amounts, isolate the vanadium with 8-hydroxyquinoline as described on p. 446.

**Note.**—The above procedure is especially intended for samples with low vanadium contents. If the percentage of vanadium is greater than 0.1, other procedures may be used. For example, the steel may be dissolved in sulfuric acid, and nitric acid added to oxidize iron. Vanadium may then be oxidized by adding ammonium persulfate and boiling, and determined by the peroxide method by comparison against a similar

<sup>18</sup> G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, *Chemical Analysis of Iron and Steel*. Wiley, New York, 1931; p. 74.

<sup>19</sup> The directions for the sodium bicarbonate precipitation are those of Lundell, Hoffman and Bright, *loc. cit.*, p. 300.

standard solution. If titanium is present, both vanadium and it can be determined by obtaining the extinction at two suitable wave lengths (see p. 425). Molybdenum should not be present in appreciable amounts. Much chromium will make necessary a separation of it and vanadium. See also the procedure given by Wright and Mellon (*loc. cit.*) for the determination of vanadium in steel.

### C. BIOLOGICAL MATERIALS

The determination of minute amounts of vanadium in this class of materials is best made by ashing the sample and then treating the ash as described under "Silicate Rocks," p. 445.

## CHAPTER XLVIII

### ZINC

#### I. Separations

Isolation of zinc by precipitation as sulfide is sometimes of value in trace analysis; this method was commonly used before the introduction of dithizone. In ammoniacal solution the precipitation of zinc sulfide is easily effected, and if tartrate is present, separation can be made from aluminum, titanium, etc.; iron, manganese, nickel, cobalt, and other sulfide-forming metals accompany the zinc. Precipitation of zinc sulfide in very dilute acid solution, the procedure so useful in ordinary analysis, is incomplete for traces unless a collector is used. By using 0.5 mg. of copper as collector, quantities of zinc of the order 0.01 mg. can be completely precipitated from 10 ml. of an acetic acid-acetate solution neutral to methyl orange.<sup>1</sup> Mercuric sulfide may also be used as collector; it is easily eliminated by ignition. Small amounts of copper (some milligrams) can be precipitated in 0.2–0.3 *N* hydrochloric acid solution without serious loss of zinc from the solution, but with large amounts, an appreciable fraction of the zinc will be removed from the solution by co- or post-precipitation.

The use of dithizone (p. 72) provides an easy way of isolating zinc in its determination in silicates, biological materials, water, etc. The simplest procedure involves the extraction of zinc from a weakly ammoniacal solution containing citrate or tartrate to prevent the precipitation of iron, aluminum, and other metals. Other metals reacting with dithizone should not be present in large amounts, for an impractically large volume of dithizone will then be required for extraction. This condition is fulfilled in the case of the samples mentioned. The simplest way of recovering the zinc from the carbon tetrachloride or chloroform solution consists in shaking the latter with dilute mineral acid (0.01–0.02 *N*) to decompose zinc dithizonate and transfer zinc to the aqueous phase.

The value of the equilibrium constant of zinc dithizonate in chloroform is approximately 3 (p. 77). If a 0.0002 *M* zinc dithizonate solution (corresponding to 0.01 per cent or 0.0004 *M* dithizone) is shaken with 0.01 *N*

<sup>1</sup> R. E. Lutz, *J. Ind. Hygiene*, 7, 273 (1925). For the separation of zinc from much iron by hydrogen sulfide precipitation in citrate medium at pH 2.5 see H. A. Bright, *Bur. Standards J. Research*, 12, 383 (1934).

hydrochloric acid, the ratio of concentration of zinc in the chloroform and aqueous phases at equilibrium will be:

$$\frac{[\text{ZnDz}'_2]_{\text{CHCl}_3}}{[\text{Zn}^{++}]_{\text{H}_2\text{O}}} = K \frac{[\text{Dz}]^2_{\text{CHCl}_3}}{[\text{H}^+]^2} = \frac{3 \times 16 \times 10^{-8}}{10^{-4}} = 0.005.$$

Accordingly if the volume of acid is somewhere near that of the chloroform, most of the zinc will be found in the aqueous phase. The small remaining fraction of zinc in the chloroform can be nearly completely removed by shaking with a fresh portion of acid. This conclusion has not been verified experimentally in the case of a chloroform solution of zinc dithizonate but it has been shown that a carbon tetrachloride solution of zinc dithizonate<sup>2</sup> can be decomposed quantitatively in this way. Cupric dithizonate in carbon tetrachloride is hardly affected by shaking with 0.01 *N* acid, which is in accord with the large value (*ca.*  $10^{10}$ ) for the equilibrium constant of this complex (see further p. 81). Lead, cadmium, and to some extent, bismuth accompany zinc into the acid phase. Cobalt dithizonate is but slightly decomposed by dilute hydrochloric acid and practically all of it remains in the carbon tetrachloride. Nickel dithizonate is partially decomposed by weak mineral acids.

The separation of much copper from zinc is perhaps most expeditiously accomplished by electrolysis. Large amounts of iron can be separated by ether extraction of ferric chloride from a hydrochloric acid solution.<sup>3</sup>

## II. Methods of Determination

### A. THE DITHIZONE METHOD

Dithizone is the only reagent at present that permits a satisfactory direct colorimetric determination of zinc.

Zinc reacts readily with dithizone in weakly alkaline medium to form the keto complex which is soluble in carbon tetrachloride or chloroform, giving a solution of bright red color. In weakly acid solution the reaction is more or less complete, depending upon the concentration of dithizone in the organic solvent according to the relation given above.

Since many other metals react with dithizone under the same conditions as zinc, it is necessary to use a complex-forming agent to prevent the interference of these. At a *pH* of 4 to 5.5, sodium thiosulfate largely prevents the reaction of copper, mercury, silver, gold, bismuth, lead, and cadmium with dithizone while permitting that of zinc to proceed.<sup>4</sup> In the presence of much nickel and cobalt it is necessary to use potassium cyanide as a

<sup>2</sup> The equilibrium constant of zinc dithizonate in carbon tetrachloride has not been determined.

<sup>3</sup> H. A. Bright, *Bur. Standards J. Research*, **12**, 383 (1934).

<sup>4</sup> H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **107**, 241 (1937).



complex forming agent. Sodium diethyldithiocarbamate has also been used as a general complex former in ammoniacal solution in the determination of zinc after removal of copper.<sup>5</sup>

Zinc, like other heavy metals, can be determined by the mixed-color or mono-color method, and depending on conditions one or the other may be preferable. If only traces of other metals reacting with dithizone are present so that relatively little thiosulfate need be added, then the mixed color procedure may be applied to advantage. But if high concentrations of interfering metals are present this method cannot readily be applied directly because there may be slight reaction between the foreign metals and dithizone which can be prevented in the mono-color method. Much thiosulfate reduces the sensitivity of the mixed-color method owing to the formation of a weak zinc thiosulfate complex.

TABLE 61

DETERMINATION OF ZINC BY THE MIXED COLOR METHOD IN THE PRESENCE OF SOME FOREIGN METALS (RED FILTER)

2.00  $\gamma$  zinc taken in each determination

Foreign metal, $\gamma$ .....	500 Pb	1000 Fe <sup>III</sup>	5 Cu	250 Bi	250 Cd
Zn found, $\gamma$ .....	2.1	2.18	2.2	3.0	3.1
Foreign metal, $\gamma$ .....	300 Co, 300 Ni		500 Ni	(2.0 ml. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> )	
Zn found, $\gamma$ .....	5.1		2.8	1.35	

### 1. The Mixed-Color Method

This method is readily applied in the determination of zinc in rocks, biological samples, water, etc., and is used in preference to the mono-color method whenever possible, *i.e.*, whenever relatively large amounts of dithizone-reacting metals are not present. If copper is first separated the mixed-color method may be used for the materials mentioned with assurance of correct results. The effect of some foreign metals in this method is indicated in Table 61. It will be noted that lead has practically no effect, nickel considerably more, while copper may be present in very small amounts only (about twice that of zinc). By the addition of more thiosulfate the permissible limits of these metals can be increased, but then the sensitivity of the zinc reaction is decreased as already mentioned.

The concentration of zinc dithizonate in the carbon tetrachloride solution may be found directly by measuring the transmittancy with a green filter, or alternatively indirectly by obtaining the concentration of the remaining dithizone from the measurement of the transmittancy with a red filter.

<sup>5</sup> E. B. Holland and W. S. Ritchie, *J. Assoc. Official Agr. Chem.*, **22**, 333 (1939); H. Cowling and E. J. Miller, *Ind. Eng. Chem., Anal. Ed.*, **13**, 145 (1941). Only small amounts of cadmium may be present in this method.

The deviation from linearity shown in Fig. 71 is at least in part to be attributed to the use of insufficiently selective filters.

### Reagents

*Dithizone*, 0.001 per cent (weight/volume) in pure carbon tetrachloride.

*Acetate buffer*, pH ca. 4.75. Mix equal volumes of 2 *N* sodium acetate and 2 *N* acetic acid, and remove reacting heavy metals by shaking with 0.005 or 0.01 per cent dithizone solution. Filter through a small quantitative paper to remove droplets of carbon tetrachloride.

*Sodium thiosulfate*, 25 g. of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 100 ml. of water.

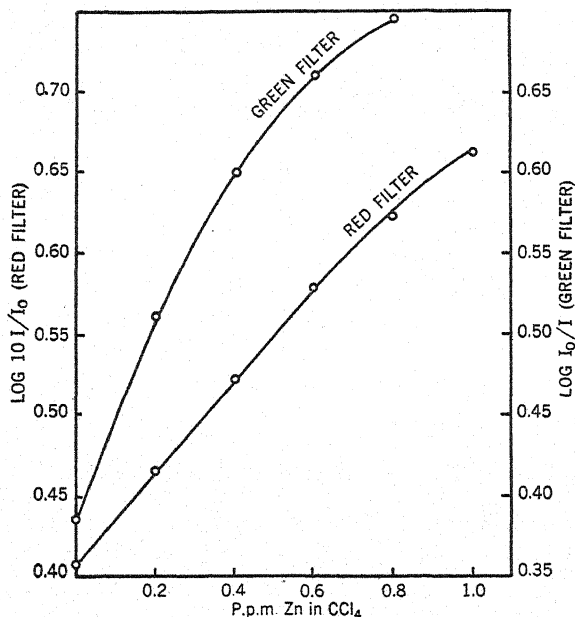


Fig. 71.—Determination of zinc with dithizone by the mixed-color method (1 cm. layer of solution).

*Standard zinc solution*, 0.01 per cent in ca. 0.1 *N* hydrochloric acid. Dissolve reagent-grade 30-mesh zinc in a slight excess of hydrochloric acid and dilute to volume. From this solution prepare by dilution with pure water a 0.001 per cent zinc solution in 0.01–0.02 *N* hydrochloric acid.

### ¶ Procedure

To 10 ml. of solution<sup>6</sup> only slightly acid (0.01–0.03 *N*) and containing less than 5  $\gamma$  of zinc, which has been transferred to a small separatory fun-

<sup>6</sup> The volume of the sample may be larger—say 20 ml.—but then correspondingly larger volumes of buffer and thiosulfate should be added. The volume should be known within 1 or 2 ml. so that the standards for the construction of the calibration curve can be diluted to the same volume (the concentration of thiosulfate affects the zinc ion concentration and therewith the color given with a constant amount of dithizone).

nel, add 5.0 ml. of buffer solution ( $pH$  4.75) and 1.00 ml. of sodium thiosulfate solution. Mix and shake vigorously for 2 minutes with 5.0 ml. of 0.001 per cent dithizone in carbon tetrachloride. Dry the stem of the funnel with filter paper and run the clear carbon tetrachloride solution into a covered cell. Obtain the transmittancy of the solution with light of either 520–540 or 620  $m\mu$  wave length (*cf.* Fig. 71).

**Visual Comparison.**—The procedure is very similar to that just described. It is advantageous to determine first the approximate amount of zinc in the sample solution which has been diluted to a definite volume (conveniently 25 ml.). To do this, transfer 1 or 2 ml. of the solution to a flat-bottomed glass-stoppered tube (p. 42), add 2–3 ml. of water, enough acetate buffer to make the  $pH$  4.5–4.75 and 5 drops of sodium thiosulfate solution. Shake for a minute with 5 ml. of 0.001 per cent dithizone. The colors given by various amounts of zinc are approximately the following: 1  $\gamma$ , blue; 2  $\gamma$ , purple-violet; 3  $\gamma$ , violet; 4–5  $\gamma$ , red-violet.

Transfer an aliquot containing 2–4  $\gamma$  of zinc to a color comparison tube, add sufficient acetate buffer to maintain the  $pH$  practically constant, and 1.00 ml. of sodium thiosulfate (for a total volume of 10–15 ml.). Shake well for 2 minutes with 5.0 ml. of 0.001 per cent dithizone and compare against a series of standards, each having the same volume and containing the same amount of thiosulfate and acetate buffer as the sample solution. Examine the carbon tetrachloride layers transversely against a white background in good light. The adjacent members of the standard series may conveniently differ by 0.5  $\gamma$  of zinc.

When the sample contains less than 1–2  $\gamma$  of zinc, reduce the volume of dithizone to 1 or 2 ml. A few tenths of a microgram of zinc can then be determined with considerable precision.

## 2. The Mono-Color Method

A solution of sodium sulfide, instead of ammonia or other base, is used to remove the excess of dithizone in this method, because traces of zinc in the sulfide solution will not react with the excess of reagent, as would happen if ammonia were used (zinc is a common impurity in ammonia and other alkalies). Before the removal of the excess dithizone, the carbon tetrachloride extract is washed with sodium thiosulfate solution to decompose any small amounts of dithizonates of foreign metals. Zinc dithizonate in carbon tetrachloride obeys Beer's law.

The directions given below for the mono-color method are those of Fischer and Leopoldi. Some representative results obtained in the application of the procedure are contained in Table 62. Traces of zinc are readily determined in this way in the presence of iron, lead, silver, etc., even at ratios of foreign metal to zinc of 10,000:1. The determination is more difficult in the presence of copper, bismuth, and mercury, because of the

large amount of thiosulfate required to prevent these metals from reacting (*cf.* below). Still it is possible to determine 10  $\gamma$  of zinc in the presence of 10 mg. of these metals. Relatively little cadmium (*ca.* 0.1 mg.) may be present. Tin interferes in the stannous state but not in the stannic; large amounts of tin are best eliminated by volatilization as the bromide (see p. 456).

#### Reagents

*Dithizone*, 0.005 per cent (weight/volume) in carbon tetrachloride.

*Sodium acetate solution*, 0.5 *M*. Free the solution from heavy metals by shaking with successive small portions of 0.005 or 0.01 per cent dithizone solution, and filter through a small moistened filter paper to remove droplets of carbon tetrachloride.

*Sodium thiosulfate solution*, 50 g.  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 100 ml. of water.

*Sodium thiosulfate-acetate wash solution*. Mix 225 ml. of 0.5 *M* sodium acetate solution, 10 ml. of 50 per cent sodium thiosulfate solution, and 40 ml. of 10 per cent nitric acid, and add water to make 500 ml. Remove traces of zinc by shaking with dithizone.

*Potassium cyanide*, 5 g. in 100 ml. of water.

*Sodium sulfide wash solution*. Dilute 40 ml. of a 1 per cent sodium sulfide stock solution with 1 liter of water.

*Standard zinc solution*. See p. 452.

#### ¶ Procedure

The solution may have a volume of 10–25 ml. and should preferably contain 5  $\gamma$  or more of zinc. The sample should be only slightly acid (say 0.1 *N* in hydrochloric acid). If much acid is present it is preferably removed by evaporation (best in a silica dish); neutralization is usually less advisable because it may introduce appreciable quantities of zinc.

Add sodium acetate solution to give a pH of 5 to 5.5 (bromocresol green may be used as indicator). Next add sufficient sodium thiosulfate to form complexes with the interfering metals. The amount of thiosulfate to be added depends on the interfering element and its quantity. For each milligram of foreign metal the following amounts (milligrams) of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  are required:

Cu	500–600
Hg	650–750
Bi	300–350
Ag	50–60
Pb	32–40

Shake the solution vigorously with 2–3 ml. of 0.005 per cent dithizone for about a minute, draw off the extract into another separatory funnel, and wash the first with 0.5–1 ml. of carbon tetrachloride. Repeat the extraction until the last portion of dithizone remains unchanged in color after shaking for 2 to 3 minutes.

Wash the combined carbon tetrachloride extracts two or three times with 5 ml. portions of sodium thiosulfate-acetate wash solution. Then wash once with water and two or three times with 5 ml. portions of sodium sulfide solution. The last portion of sulfide wash solution must remain colorless.

Dilute the washed zinc dithizonate solution to a definite volume with carbon tetrachloride and obtain the transmittancy of the solution at 535 m $\mu$ , or compare against a similar standard solution obtained in the same way. Run a blank through the whole procedure.

TABLE 62  
DETERMINATION OF ZINC WITH DITHIZONE BY THE MONO-COLOR METHOD<sup>7</sup>

Foreign Metal	Zn taken $\gamma$	Zn found $\gamma$	Error $\gamma$
	6.2	6.0	-0.2
	4.1	4.1	0.0
	37.4	36.8	-0.6
50 mg. Fe (III)	6.2	7.3	+1.1
100 mg. Mn	6.2	6.3	+0.1
10 mg. Cu	8.3	8.8	+0.5
100 mg. Ag	16.6	16.2	-0.4
125 mg. Pb	8.3	8.7	+0.4
0.07 mg. Cd	12.4	12.8	+0.4
150 mg. Sn <sup>a</sup>	16.6	16.9	+0.3
100 mg. Al <sup>b</sup>	6.2	7.0	+0.8
100 mg. Ni <sup>c</sup>	6.3	6.0	-0.3
100 mg. Co <sup>c</sup>	6.4	6.8	+0.4

<sup>a</sup> Sn volatilized with Br<sub>2</sub> + HBr.

<sup>b</sup> Double extraction.

<sup>c</sup> In the presence of KCN.

**Notes.**—1. In the presence of appreciable amounts of nickel and cobalt proceed as follows. Approximately neutralize the solution with pure ammonia and add enough 5 per cent potassium cyanide solution to dissolve the precipitate first formed. Add dilute hydrochloric acid dropwise until the pH is 3 to 4, and then adjust the pH to 5-5.5 with sodium acetate. Extract the clear solution with dithizone as described above. Fourteen ml. of 5 per cent potassium cyanide are sufficient to tie up 100 mg. of either nickel or cobalt.

It is also possible to carry out the determination of zinc in the presence of nickel (Zn:Ni > 1:1000) by making a double extraction as follows. Extract the thiosulfate-containing solution with dithizone until a brownish-green color is obtained (due to nickel which reacts after zinc), and then shake the combined extracts, which have been washed with water, with two 5 ml. portions of 0.1 N hydrochloric acid to bring zinc

<sup>7</sup> Representative data of H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **107**, 241 (1937).

into the aqueous phase. Adjust the pH of the acid extract to 5-5.5 and determine zinc in the usual way. In the presence of much thallium a similar double extraction should be made.

2. If tin is present in the sample volatilize it by adding 5 ml. of bromine-hydrobromic acid mixture (20 ml.  $\text{Br}_2$  + 100 ml.  $\text{HBr}$ ) and evaporating to dryness on the steam bath. Treat the residue with 1 ml. of aqua regia, evaporate to dryness, and dissolve the residue in 0.5 ml. of 10 per cent nitric acid.

3. Aluminum hinders the extraction of zinc from slightly acid solution, and if it is present in amounts greater than 100 mg., it is necessary to extract zinc from a faintly ammoniacal solution containing citrate or tartrate. Large amounts of other reacting heavy metals can then not be present, for too much dithizone would be required for extraction. The extract containing zinc and other reacting metals is shaken with dilute hydrochloric acid (e.g., 0.1  $N$ ) to bring zinc into the aqueous phase, in which it is then determined according to the above procedure.

4. Large amounts of cadmium will react with dithizone in spite of the presence of thiosulfate. As much as 70  $\gamma$  of cadmium may be present however if the zinc dithizonate extract is washed 5-6 times with sodium sulfide to remove cadmium completely (Table 62).

5. Instead of using thiosulfate to prevent the reaction of copper, mercury, and silver (and probably gold and palladium), these metals may be precipitated with hypophosphite in acid solution. Add 1 or 2 ml. of 10 per cent sodium hypophosphite solution to 10 or 20 ml. of sample solution acidified slightly with mineral acid, heat to boiling, and keep at the boiling point for a few minutes until the precipitate has coagulated. Filter the solution, wash with water, and extract the filtrate and washings with dithizone solution to remove traces of unprecipitated metals. Then determine zinc, after adjusting the acidity of the solution, by either the mono- or mixed-color method. The results with 10 mg. of copper, 15 mg. of mercury, and 100 mg. of silver are low to the extent of 5-10 per cent for zinc quantities ranging from 6 to 33  $\gamma$ , owing to slight coprecipitation of zinc.

## B. OTHER METHODS

In weakly alkaline alcoholic solution, urobilin or stercobilin gives a strong green fluorescence with zinc. As little as 1  $\gamma$  of zinc can be detected in ultraviolet light. Many metals interfere, even if present in minute amounts only, but after isolation zinc can be determined satisfactorily with urobilin.<sup>8</sup>

Zinc can be determined nephelometrically or turbidimetrically as the ferrocyanide<sup>9</sup> or the sulfide.<sup>10</sup>

Zinc may be precipitated with 8-hydroxyquinoline and determined by an indirect colorimetric method (cf. p. 95).<sup>11</sup> In another indirect method, zinc is precipitated with 5-nitroquinaldic acid and the precipitate reduced with stannous chloride to give an orange water-soluble compound.<sup>12</sup>

<sup>8</sup> R. E. Lutz, *J. Ind. Hygiene*, **7**, 273 (1925).

<sup>9</sup> L. T. Fairhall and J. R. Richardson, *J. Am. Chem. Soc.*, **52**, 938 (1930); H. M. Boggs and A. O. Alben, *Ind. Eng. Chem., Anal. Ed.*, **8**, 97 (1936).

<sup>10</sup> L. W. Winkler, *Z. angew. Chem.*, **26**, 38 (1913); L. Pincussen and E. Brück, *Biochem. Z.*, **265**, 58 (1933).

<sup>11</sup> M. Teitelbaum, *Z. anal. Chem.*, **82**, 366 (1930).

<sup>12</sup> W. L. Lott, *Ind. Eng. Chem., Anal. Ed.*, **10**, 335 (1938).

### III. Applications of the Dithizone Method

#### A. SILICATE ROCKS

The mixed-color dithizone method is the most suitable one for the determination of zinc in rocks. All the reacting metals of the sample are first isolated by extracting the ammoniacal citrate solution of the decomposed rock with dithizone in carbon tetrachloride. The extract is then shaken with very dilute hydrochloric acid (0.01–0.02 *N*) to obtain zinc, lead, etc., in the aqueous phase; copper, and most of the cobalt and nickel remain in the carbon tetrachloride. Zinc can then be determined in the aqueous solution after adjusting the *pH* and adding thiosulfate.<sup>13</sup>

TABLE 63  
DETERMINATION OF ZINC IN SILICATE ROCKS BY THE DITHIZONE METHOD

Sample	Zinc present per cent	Zinc found per cent
Acid rock (synthetic)	0.0024	0.0026
Acid rock (synthetic)	0.004	0.0045
Acid rock (synthetic)	0.007	0.007
Acid rock (synthetic)	0.0115	0.012
Basic rock (synthetic)	0.0105	0.010
Basic rock (synthetic)	0.015	0.015
Basic rock (synthetic)*	0.005	0.006

\*Contained 0.05% Cu, 0.1% Pb, 0.2% Ni, and 0.05% Co.

#### Reagents

See p. 294.

#### ¶ Procedure

Decompose 0.25 g. of sample with perchloric and hydrofluoric acids as described on p. 295, and if any appreciable amount of insoluble material remains treat as there described. Extract the dithizonates from the ammoniacal citrate solution and shake the extract with 0.02 *N* hydrochloric acid (p. 296).

Make up the hydrochloric acid solution containing the zinc to 25 ml. in a volumetric flask. Take 5 ml. (for less than 0.01 per cent zinc) or 2 ml. (for 0.01–0.025 per cent) of the solution for analysis. Add 2 ml. of acetate buffer and 0.5 ml. of sodium thiosulfate (see p. 452) and shake with 5 ml. of 0.001 per cent dithizone for 2 minutes. Determine the transmittancy of the carbon tetrachloride solution (p. 453) or compare against a series of standards prepared in the same manner as the sample solution (p. 453). Correct the result for zinc in the reagents.

<sup>13</sup> E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **9**, 464 (1937).

B. SOILS<sup>14</sup>

For the determination of total zinc in soils, a procedure very similar to that given above for silicate rocks may be used. If much organic matter is present it may be advisable to treat the finely-ground sample first with a few milliliters of concentrated nitric acid, evaporate to dryness and then decompose with perchloric and hydrofluoric acids. The rest of the procedure is the same as in A above, except that a smaller aliquot may be necessary, since the zinc content of soils may rise to 500 p.p.m.

## C. WATER

## ¶ Procedure

Add 5 ml. of 10 per cent sodium (or ammonium) citrate to 50 ml. of sample and if the solution is not already basic, make it weakly ammoniacal. Shake with small portions of 0.01 per cent dithizone in carbon tetrachloride until the latter does not turn violet or bluish but remains green. Combine the extracts, wash the carbon tetrachloride with a few milliliters of water and shake thoroughly with 10 ml. of 0.02 *N* hydrochloric acid to transfer the zinc to the aqueous phase. Draw off the carbon tetrachloride into another separatory funnel and shake with a fresh 5 or 10 ml. portion of 0.02 *N* acid to be certain that all the zinc has been removed. Dilute the acid extracts to 25 or 50 ml. in a volumetric flask, and determine zinc in a 10 ml. aliquot according to the mixed color method, p. 452.

**Note.**—If copper does not greatly exceed zinc ( $\text{Cu/Zn} < 2$ ) and excessive amounts of iron are not present, zinc may be determined directly in 10 ml. of the sample after adjustment of the *pH* and addition of thiosulfate as described on p. 452.

When very minute traces of zinc are to be determined in water, a suitable amount of acidified sample should be evaporated to a small volume in a silica or platinum disk. Sodium citrate is then added and zinc isolated as described above.

## D. BIOLOGICAL MATERIALS

After ashing, zinc may be determined in biological samples in essentially the same way as in silicate rocks, *i.e.*, all the reacting metals are extracted with dithizone from ammoniacal citrate solution and the carbon tetrachloride extract is shaken with 0.02 *N* hydrochloric acid to bring zinc into the aqueous phase, in which it is determined with dithizone by the mixed-color method after adjustment of the *pH* and addition of sodium thiosulfate to prevent the reaction of traces of lead, cadmium, etc.

Organic material may be destroyed by ignition or by digestion with

<sup>14</sup> See also G. D. Sherman and J. S. McHargue, *J. Assoc. Official Agr. Chem.*, **25**, 510 (1942). These authors recommend fusion of the soil sample with sodium-potassium carbonate (3 g. of mixed carbonates for 0.5 g. sample). Silica is dehydrated and separated in the usual manner.



acids. According to Lutz and Thompson<sup>15</sup> dry ashing gives entirely satisfactory results. One advantage of dry ashing is the smaller blank associated with it. The digestion method may require neutralization of the acid in the mixture with ammonia or other base, and appreciable amounts of zinc may thus be introduced unless the ammonia is redistilled and then stored in a wax-lined bottle.

### Special Solutions

*Dithizone*, 0.01 per cent in carbon tetrachloride.

*Hydrochloric acid*, 6 *N*. Redistilled acid is preferable but not essential.

*Hydrochloric acid*, 0.02 *N*. Use redistilled water in diluting.

*Ammonia*, concentrated aqueous solution. Ammonium hydroxide is likely to contain relatively much zinc and should be distilled; alternatively absorb the gas from a tank in pure water. The purified solution should be kept in a ceresin-coated bottle.

*Sodium citrate*, 10 per cent. Dissolve 10 g. of the citrate in 100 ml. of water, make faintly ammoniacal, and remove reacting heavy metals by shaking with small portions of 0.01 per cent dithizone until the carbon tetrachloride remains green. Filter through a small paper previously washed with dilute hydrochloric acid to remove droplets of carbon tetrachloride. Keep the purified solution in a ceresin-coated bottle.

### Procedure

If the material contains more than 2-3 p.p.m. of zinc, a 1 gram sample is sufficient. Ash in a silica or platinum dish at a temperature below 500°. Add a mixture of 2-3 ml. 6 *N* hydrochloric acid and an equal volume of water to the ash and heat at the boiling point until all soluble material has been brought into solution. Filter through a small paper which has previously been washed with hot dilute hydrochloric acid to remove traces of zinc. Wash with warm water. If particles of carbon are visible in the residue, ignite the paper and its contents as before and extract the residue with a little dilute hydrochloric acid.<sup>17</sup>

Add 5 ml. of sodium citrate to the filtrate and washings (volume about 20 ml.), make ammoniacal (litmus), and add an excess of 0.2-0.3 ml.<sup>18</sup> Extract in a separatory funnel with a few milliliters of 0.01 per cent dithizone solution and transfer the carbon tetrachloride to another separatory

<sup>15</sup> R. E. Lutz, *J. Ind. Hygiene*, 7, 279 (1925); P. K. Thompson, *ibid.*, 7, 358 (1925).

<sup>16</sup> Cf. p. 168. If the addition of nitric acid or magnesium (potassium) nitrate is deemed necessary for easier oxidation of carbon, the amount added should be noted so that a like amount can be included in the blank.

<sup>17</sup> If an appreciable amount of residue insoluble in hydrochloric acid remains, it should be hydrofluorized or otherwise treated (fusion with sodium carbonate) to bring it into solution. L. H. Rogers and O. E. Gall, *Ind. Eng. Chem., Anal. Ed.*, 9, 42 (1937), have shown that zinc may be present in hydrochloric acid-insoluble material.

<sup>18</sup> If the solution becomes appreciably turbid, allow it to stand for half an hour, filter off the precipitate, fuse it with sodium carbonate, and treat further as described on p. 295.

funnel. Repeat the extraction with more dithizone until the last portion remains green after shaking for at least one-half minute.

Shake the combined carbon tetrachloride extracts for 2 minutes with 10 ml. of 0.02 *N* hydrochloric acid, transfer the latter to a 25 ml. volumetric flask, and shake the carbon tetrachloride solution with a fresh 10 ml. portion of the dilute hydrochloric acid to insure the removal of all the zinc. Add the aqueous solution to the flask and make up to 25 ml. with water. Depending upon the amount of zinc expected, take a 10 ml. aliquot (1–5  $\gamma$ ) or less, and proceed as described in the general procedure p. 452.

**Note.**—If it is desired to use a digestion method in destroying organic matter, follow the directions on p. 278.

*Addendum during proof-reading.* For a method of determining zinc in biological material involving the use of di- $\beta$ -naphthylthiocarbazone see J. Cholak, D. M. Hubbard, and R. E. Burkey, *Ind. Eng. Chem., Anal. Ed.*, **15**, 754 (1943).

## CHAPTER XLIX

### ZIRCONIUM

#### I. Separations

The very low solubility of zirconium dihydrogen phosphate in 1:10 hydrochloric or sulfuric acid enables small quantities of zirconium to be precipitated as such and separated from most metals.<sup>1</sup> When titanium is present, hydrogen peroxide must be added to prevent its precipitation. The precipitate can be fused with sodium carbonate and the melt leached with water to separate phosphate. All traces of phosphate must be eliminated by thorough washing before dissolving the residue in hydrochloric or dilute perchloric acid.

Phenylarsonic and other arsonic acids yield slightly soluble precipitates with zirconium in acid solution,<sup>2</sup> but their value for the separation of traces of zirconium remains to be proven.

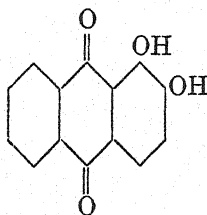
Cupferron is a useful precipitant for zirconium in certain cases. Ferric iron can be used as a collector.<sup>3</sup>

Large amounts of iron can be separated from zirconium by ether extraction of ferric chloride or by electrolysis with a mercury cathode.

#### II. Methods of Determination

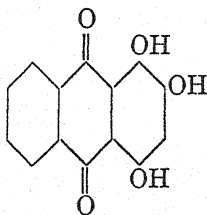
##### A. THE ALIZARIN METHOD \*

Under suitable conditions it is possible to determine small amounts of zirconium (and hafnium) by the use of various hydroxyanthraquinones such as:



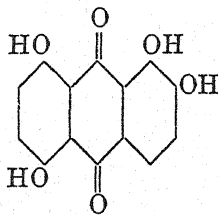
Alizarin

1,2-Dihydroxyanthraquinone



Purpurin

1,2,4-Trihydroxyanthraquinone



Quinalizarin

1,2,5,8-Tetrahydroxyanthraquinone

<sup>1</sup> According to G. von Hevesy, *Chemical Analysis by X-rays and Its Applications*. Cornell Univ. Press, Ithaca, 1932; p. 211, the solubility of zirconium phosphate,  $\text{ZrO} \cdot (\text{H}_2\text{PO}_4)_2$ , in 6.0 *N* hydrochloric acid corresponds to 3.3 mg.  $\text{ZrP}_2\text{O}_7$  or 1.1 mg. Zr

These dyes form slightly soluble, strongly colored lakes with most cations at the proper acidities; the color of the lake is different from that of the dye itself. The zirconium lake is stable at relatively high acidities in contrast to most of the other metal lakes. In alcoholic medium fairly stable suspensions of the zirconium lake can be obtained which are suitable for photometric use.<sup>4</sup>

For general use, alizarin is the most suitable of the three hydroxyanthraquinones mentioned. It gives a lake which follows Beer's law rather closely up to a concentration of at least 4 p.p.m. of zirconium (Fig. 72). The other two reagents (especially quinalizarin) give colored products which show large deviations from Beer's law. Quinalizarin, however, is 2-3 times as sensitive a reagent as alizarin. The failure of the purpurin lake to conform to Beer's law has been attributed to scattering of light by the relatively large particles composing it. The alizarin lake has the smallest particle size of the three, and when first formed may exist in true solution. Eventually the alizarin lake settles out, but it can be redispersed by shaking, and the transmission curve of such a suspension is but little different from one freshly prepared.

The final acidity of the solution affects the color intensity considerably. With 50  $\gamma$  of zirconium under the conditions described in the procedure below, the minimum transmittancy at 560  $\mu$  is obtained with 0.05 ml. of 12 *N* hydrochloric or perchloric acid in excess; with no acid and with 0.5 ml. in excess there is an increase in transmission corresponding in both cases to an error of  $-4.2 \gamma$ , and with 1 ml. acid in excess the error is  $-11.6 \gamma$ .

Fluoride, sulfate, phosphate, and organic hydroxy acids decrease or destroy the color of the zirconium compound because of the formation of very stable complexes with zirconium. Molybdate and tungstate have a like effect.

The effect of cations on the determination of zirconium has not been thoroughly investigated, but it appears that in general only limited amounts of foreign metals may be present. Iron (III), chromium (III), and cobalt cause positive errors, the transmission being decreased without the shape of the transmission curve being greatly changed. Many cations (cadmium, copper, lead, aluminum) give rise to negative errors. The effect is more pronounced in hydrochloric than in perchloric acid solutions, and

per 100 ml. at room temperature. It may be inferred that in 1:10 hydrochloric acid in the presence of excess phosphate the solubility will be much smaller. Cf. O Hackl, *Z. anal. Chem.*, **122**, 1 (1941).

<sup>2</sup> See, for example, F. Feigl, *Specific and Special Reactions*. Nordeman, New York, 1940; p. 120.

<sup>3</sup> See the reference on p. 439.

<sup>4</sup> H. A. Liebhafsky and E. H. Winslow, *J. Am. Chem. Soc.*, **60**, 1776 (1938). The material in this section is drawn from this paper.

is apparently due to the formation of complexes such as  $\text{CdCl}_4^{2-}$  which combine with zirconyl ion. The positive error due to iron can be decreased by increasing the hydrochloric acid concentration, but then the sensitivity of the zirconium reaction is decreased. According to Liebhafsky and Winslow the error caused by the metals mentioned when present to the extent of 1 mg. should not exceed 50 per cent in most cases when 10  $\gamma$  of Zr are being determined under the conditions of the procedure following. In other words if these metals are present in amounts comparable to that of zirconium the interference should not be appreciable.

Titanium forms a lake with alizarin even in fairly strongly acid solutions and leads to high results for zirconium. The thorium lake is not easily formed when sufficient hydrochloric acid is present (2 ml. 12 *N* acid in about 25 ml.) and the interference of thorium is much less than that of titanium. Hafnium gives the same reaction as zirconium and the transmission curves of the lakes of the two elements are qualitatively identical. One gram of zirconium is spectrophotometrically equivalent on the average to 2.55 g. of hafnium (1 mole Zr  $\equiv$  1.30 moles Hf). In a known weight of a mixture of the two elements, containing no other elements, both can thus be determined indirectly, provided the ratios are not too unfavorable.

#### Special Solutions

*Alizarin*, 0.125 per cent (weight/volume) in ethyl alcohol.

*Standard zirconium solution*, 0.01 per cent Zr in 2 *N* hydrochloric acid. Prepare this solution by diluting a 0.1–0.2 per cent zirconium solution in 4 *N* hydrochloric acid. The stronger solution may be prepared from pure zirconyl chloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /Zr = 3.53) and should be standardized by precipitation with ammonia and ignition of the precipitate to zirconium oxide.

#### ¶ Procedure

Transfer 1 ml. or less of the zirconium solution (5–100  $\gamma$  Zr) in *ca.* 2 *N* hydrochloric acid to a 25 ml. volumetric flask that has been rinsed with alcohol. Add 0.50 ml. of alizarin solution and then ammonium hydroxide dropwise until the color change shows that the mixture is slightly alkaline. Allow to stand for 2 minutes, then neutralize with 1 *N* hydrochloric acid, and add 0.10 ml. of 7 *N* hydrochloric acid. Dilute to 25 ml. with alcohol and read the solution in a photometer using light of wave length 560  $m\mu$  (see Fig. 72).

#### B. THE p-DIMETHYLAMINOAZOPHENYLARSONIC ACID METHOD

Phenylarsonic acid and various derivatives yield slightly soluble precipitates with zirconium in acid solution. *p*-Dimethylaminoazophenylarsonic

acid<sup>5</sup> gives a colored precipitate which after washing can be decomposed with ammonium hydroxide and the yellow color of the resulting solution measured.<sup>6</sup> This method has been applied to the determination of zirco-

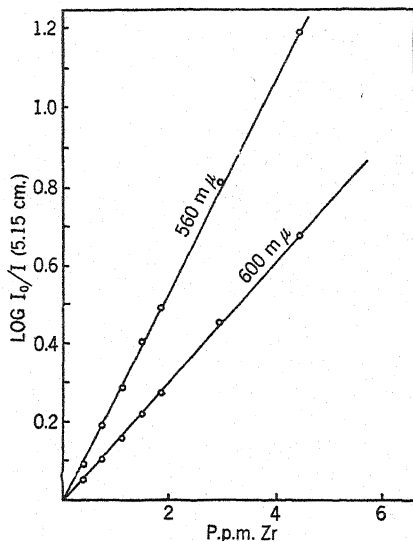


Fig. 72.—Determination of zirconium with alizarin. (From Liebhafsky and Winslow).

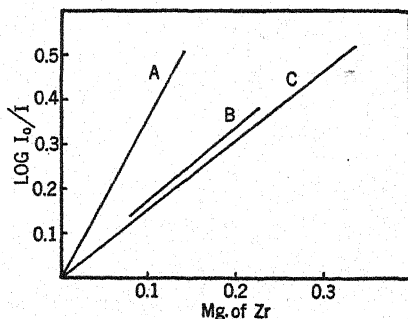


Fig. 73.—Determination of zirconium with *p*-dimethylaminoazophenylarsonic acid according to Hayes and Jones. A. More than 5  $\gamma$  Zr in 10 ml. or less of 2 *N* hydrochloric acid. B. 5  $\gamma$  Zr in 50 ml. of 2 *N* hydrochloric acid. C. Precipitation from 50 ml. of solution containing 0.1 g. iron.

nium in steel.<sup>7</sup> More data on the accuracy of the method would be desirable.

<sup>5</sup> F. Feigl, P. Krumholz, and E. Rajmann, *Mikrochemie*, **9**, 395 (1931).

<sup>6</sup> V. A. Nazarenko, *J. Applied Chem. U. S. S. R.*, **10**, 1696 (1937).

<sup>7</sup> W. G. Hayes and E. W. Jones, *Ind. Eng. Chem., Anal. Ed.*, **13**, 603 (1941).

According to Hayes and Jones the composition of the precipitate given by the azophenylarsonic acid varies with conditions. With more than 5  $\gamma$  of zirconium in 10 ml. or less of 2 *N* hydrochloric acid the precipitate probably has the composition  $\text{Zr}[(\text{CH}_3)_2\text{N} \text{---} \text{C}_6\text{H}_4 \text{---} \text{N}=\text{N} \text{---} \text{C}_6\text{H}_4 \text{---} \text{AsO}_3]_2$ , and with the same amount of zirconium in 50 ml. of 2 *N* hydrochloric acid the composition is supposed to be represented by  $(\text{ZrO})[(\text{CH}_3)_2\text{N} \text{---} \text{C}_6\text{H}_4 \text{---} \text{N}=\text{N} \text{---} \text{C}_6\text{H}_4 \text{---} \text{AsO}_3]$ .

The directions given by Hayes and Jones for the determination of zirconium in steel follow. Small amounts of phosphorus (up to 0.05 per cent) do not interfere and require no modification of the procedure. If titanium is present hydrogen peroxide must be added to prevent its precipitation by the reagent.

### ¶ Procedure

Dissolve 1 g. of steel in 50 ml. of 1:1 hydrochloric acid, dilute to 75 ml. and filter. Reserve the filtrate. Wash the residue successively with hot water, hot 1:1 hydrochloric acid, and hot water. Ignite in a platinum crucible, fuse the residue with as much potassium pyrosulfate as required, and dissolve the melt in a little water containing a few drops of sulfuric acid. Dilute the solution to about 100 ml., add a slight excess of ammonia and boil for a minute. Filter and wash the precipitate with water. Place the paper in the beaker in which the precipitation was made, add 50 ml. of 1:1 hydrochloric acid, disintegrate the paper, and boil for a minute. Filter and combine the filtrate and washings with the original filtrate that was reserved. Dilute the solution to 500 ml. in a volumetric flask.

Transfer 50 ml. of the solution to a beaker, heat to the boiling point, add 15 ml. of reagent solution (0.25 g. of *p*-dimethylaminoazophenylarsonic acid dissolved in 10 ml. concentrated hydrochloric acid + 240 ml. alcohol), and boil for one minute. Cool to room temperature and allow to stand for at least 30 minutes. Filter through a dense paper and wash with 1:100 hydrochloric acid until the washings are colorless. Decompose the precipitate into the ammonium salt of the arsonic acid by pouring 3 or 4 portions of 1:2 ammonia through the filter, and catch the solution in a 100 ml. volumetric flask. Dilute to the mark with water and determine the transmittancy of the solution with aid of a blue filter. Establish the calibration curve by adding known amounts of zirconium to a zirconium-free steel and carrying the samples through the procedure.

# APPENDIX

TABLE 64  
FOUR-PLACE LOGARITHMS

N	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	16	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	4	5	7	9	10	12	14	16
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	12	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	5	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	7	8	9	11	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	2	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	4	5	6	7	8	9	11
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9



TABLE 64—Continued  
FOUR-PLACE LOGARITHMS

N	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	6	7	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	5	6	7	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	3	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	1	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	3	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	5	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	3	3	4	4	5	6
N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

TABLE 64—Continued  
FOUR-PLACE LOGARITHMS

N	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	3	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	3	3	4	4	5	6
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	3	3	4	4	5	6
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	4	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	1	1	2	2	3	3	4	4	5
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	3	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

TABLE 65  
TRANSMISSION-EXTINCTION TABLE

100 $I/I_0$	Log $I_0/I$	100 $I/I_0$	Log $I_0/I$	100 $I/I_0$	Log $I_0/I$
99.8	0.0009	91.4	0.039	83.0	0.081
99.6	0.0017	91.2	0.040	82.8	0.082
99.4	0.0026	91.0	0.041	82.6	0.083
99.2	0.0035	90.8	0.042	82.4	0.084
99.0	0.0044	90.6	0.043	82.2	0.085
98.8	0.0052	90.4	0.044	82.0	0.086
98.6	0.0061	90.2	0.045	81.8	0.087
98.4	0.0070	90.0	0.046	81.6	0.088
98.2	0.0079	89.8	0.047	81.4	0.089
98.0	0.0088	89.6	0.048	81.2	0.090
97.8	0.0097	89.4	0.049	81.0	0.092
97.6	0.0106	89.2	0.050	80.8	0.093
97.4	0.0114	89.0	0.051	80.6	0.094
97.2	0.0123	88.8	0.052	80.4	0.095
97.0	0.0132	88.6	0.053	80.2	0.096
96.8	0.0141	88.4	0.054	80.0	0.097
96.6	0.0150	88.2	0.054	79.8	0.098
96.4	0.0159	88.0	0.055	79.6	0.099
96.2	0.0168	87.8	0.056	79.4	0.100
96.0	0.0177	87.6	0.057	79.2	0.101
95.8	0.0186	87.4	0.058	79.0	0.102
95.6	0.0195	87.2	0.059	78.8	0.103
95.4	0.0205	87.0	0.060	78.6	0.105
95.2	0.0214	86.8	0.061	78.4	0.106
95.0	0.0223	86.6	0.062	78.2	0.107
94.8	0.0232	86.4	0.063	78.0	0.108
94.6	0.0241	86.2	0.064	77.8	0.109
94.4	0.0250	86.0	0.066	77.6	0.110
94.2	0.026	85.8	0.067	77.4	0.111
94.0	0.027	85.6	0.068	77.2	0.112
93.8	0.028	85.4	0.069	77.0	0.113
93.6	0.029	85.2	0.070	76.8	0.115
93.4	0.030	85.0	0.071	76.6	0.116
93.2	0.031	84.8	0.072	76.4	0.117
93.0	0.032	84.6	0.073	76.2	0.118
92.8	0.032	84.4	0.074	76.0	0.119
92.6	0.033	84.2	0.075	75.8	0.120
92.4	0.034	84.0	0.076	75.6	0.121
92.2	0.035	83.8	0.077	75.4	0.123
92.0	0.036	83.6	0.078	75.2	0.124
91.8	0.037	83.4	0.079	75.0	0.125
91.6	0.038	83.2	0.080		

TABLE 66  
INTERNATIONAL ATOMIC WEIGHTS, 1943

Aluminum.....	26.97	Molybdenum.....	95.95
Antimony.....	121.76	Neodymium.....	144.27
Argon.....	39.944	Neon.....	20.183
Arsenic.....	74.91	Nickel.....	58.69
Barium.....	137.36	Nitrogen.....	14.008
Beryllium.....	9.02	Osmium.....	190.2
Bismuth.....	209.00	Oxygen.....	16.0000
Boron.....	10.82	Palladium.....	106.7
Bromine.....	79.916	Phosphorus.....	30.98
Cadmium.....	112.41	Platinum.....	195.23
Calcium.....	40.08	Potassium.....	39.096
Carbon.....	12.010	Praseodymium.....	140.92
Cerium.....	140.13	Protactinium.....	231
Cesium.....	132.91	Radium.....	226.05
Chlorine.....	35.457	Radon.....	222
Chromium.....	52.01	Rhenium.....	186.31
Cobalt.....	58.94	Rhodium.....	102.91
Columbium.....	92.91	Rubidium.....	85.48
Copper.....	63.57	Ruthenium.....	101.7
Dysprosium.....	162.46	Samarium.....	150.43
Erbium.....	167.2	Scandium.....	45.10
Europium.....	152.0	Selenium.....	78.96
Fluorine.....	19.00	Silicon.....	28.06
Gadolinium.....	156.9	Silver.....	107.880
Gallium.....	69.72	Sodium.....	22.997
Germanium.....	72.60	Strontium.....	87.63
Gold.....	197.2	Sulfur.....	32.06
Hafnium.....	178.6	Tantalum.....	180.88
Helium.....	4.003	Tellurium.....	127.61
Holmium.....	164.94	Terbium.....	159.2
Hydrogen.....	1.0080	Thallium.....	204.39
Indium.....	114.76	Thorium.....	232.12
Iodine.....	126.92	Thulium.....	169.4
Iridium.....	193.1	Tin.....	118.70
Iron.....	55.85	Titanium.....	47.90
Krypton.....	83.7	Tungsten.....	183.92
Lanthanum.....	138.92	Uranium.....	238.07
Lead.....	207.21	Vanadium.....	50.95
Lithium.....	6.940	Xenon.....	131.3
Lutecium.....	174.99	Ytterbium.....	173.04
Magnesium.....	24.32	Yttrium.....	88.92
Manganese.....	54.93	Zinc.....	65.38
Mercury.....	200.61	Zirconium.....	91.22

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